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Review

Strategies for enhancing low-frequency performances of triboelectric, electrochemical, piezoelectric, and dielectric elastomer energy harvesting: recent progress and challenges

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ABSTRACT

Mechanical energy harvesting transforms various forms of mechanical energy, including ocean waves, wind, and human motions, into electrical energy, providing a viable solution to address the depletion of fossil fuels and environmental problems. However, one major obstacle for the direct conversion of mechanical energy into electricity is the low frequency of the majority of mechanical energy sources ($\leq$5 Hz), resulting in low energy conversion efficiency, output power and output current. Over recent years, a numerous innovative technologies have been reported to enable improved energy harvesting utilizing various mechanisms. This review aims to present an in-depth analysis of the research progress in low-frequency energy harvesting technologies that rely on triboelectric, electrochemical, piezoelectric, and dielectric elastomer effects. The discussion commences with an overview of the difficulties associated with low-frequency energy harvesting. The critical aspects that impact the low-frequency performance of mechanical energy harvesters, including working mechanisms, environmental factors, and device compositions, are elucidated, while the advantages and disadvantages of different mechanisms in low-frequency operation are compared and summarized. Moreover, this review expounds on the strategies that can improve the low-frequency energy harvesting performance through the modulations of material compositions, structures, and devices. It also showcases the applications of mechanical energy harvesters in energy harvesting via waves, wind, and human motions. Finally, the recommended choices of mechanical energy harvesters with different mechanisms for various applications are offered, which can assist in the design and fabrication process.

1. Introduction

1.1. Background of mechanical energy harvesting

At present, the world's energy supply is largely dominated by non-renewable sources like coal, oil, and natural gas. However, due to the growing global population and the widespread use of industrialized equipment, their consumption rate is rapidly increasing, leading to the inevitability of insufficient reserves. To address the global energy shortage, researchers have been investigating renewable energy sources, such as solar [1,2], thermal [3–5], and mechanical energies [6–9]. Solar energy cannot be harvested under low or no light conditions, while the distribution of thermal energy is limited to certain areas where geothermal resources or production facilities exist. On the other hand, mechanical energy is present in various forms, including human activities, vibrations of industrial equipment, vehicles, as well as wind and waves. Wind-generated power technology has been extensively utilized to generate electricity in remote or isolated regions by converting wind energy into rotational mechanical energy that drives windmills, to generate electrical energy. Similarly, hydroelectric technology is employed in rivers and lakes to convert the kinetic energy of water into rotational mechanical energy to generate electricity. Researchers are also developing technologies to efficiently convert the energy produced by human movements and into electrical energy to power wearable devices, such as smart watches [10–14].

A device that can capture mechanical energy and convert it into electrical energy is known as a mechanical energy harvester. When applied to the harvester, a portion of the mechanical energy is converted into the kinetic energy of the harvester, while the remaining energy is dissipated into the surrounding environment as thermal energy. The movement of the harvester results in the movement of

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its various components, which generates an electrical potential that drives charge in an external circuit, ultimately creating electrical energy. Performance metrics such as output voltage, current, power, and energy conversion efficiency are critical aspects of mechanical energy harvesters. Output power is the ratio of the output voltage squared to resistance, while energy conversion efficiency is the ratio of the output electrical energy to the input mechanical energy. These metrics play a significant role in assessing the efficiency of energy conversion and, thus, the feasibility of mechanical energy harvesting.

1.2. Challenges for the low-frequency mechanical energy harvesters

1.2.1. Features of low-frequency mechanical energy

Mechanical movements occur at various frequencies, typical below 100 Hz [15], but a large portion of mechanical movements in our daily life occur below 5 Hz, including wind, waves, and various human activities, such as walking, running, heartbeat, and swimming (Fig. 1a–f).

In addition, low-frequency mechanical motions typically have low amplitudes [20]. For example, waves in calm oceanic regions typically have amplitudes of only a few centimeters, and the vertical foot displacement during walking for an average-sized person is typically between 10 and 20 cm. The low amplitudes of low-frequency mechanical motions result in relatively low amounts of generated mechanical energy generated, which poses a challenge in capturing and converting these motions into electrical energy. This limitation is the primary reason for the poor performance of energy harvesters at low frequencies. Furthermore, the natural frequency of the device is usually higher than the frequency of the external environment, leading to a mismatch that decreases the triggering of the device to produce electrical energy output. Consequently, this mismatch results in low energy conversion efficiency [21,22]. This issue is referred to as "frequency mismatch". Since output performances, such as power and current, are closely linked to the frequency of mechanical movement, energy harvesters designed for lower frequencies generally exhibit poor performance in terms of output power and current, due to the lower energy levels associated with these frequencies.

1.2.2. Recent progress of developing low-frequency energy harvesters

To address the challenges associated with low output performance at low frequencies, extensive research has been conducted to develop a range of energy harvesting techniques, including electromagnetic, electrochemical, triboelectric, piezoelectric, and dielectric elastomer principles [16–19]. For instance, electromagnetic energy harvesters utilize Faraday's Law to generate electrical power by converting the time-rate change of magnetic flux in a coil. However, at low frequencies, the low rotor speed of electromagnetic harvesters results in reduced output performance. While increasing magnetic field strength or coil length may enhance the performance, this also adds mass and, further decrease frequency and amplitude motion. This fundamental limitation is a challenge for electromagnetic harvesters when applied to low-frequency mechanical energy harvesting. On the other hand, electrochemical, triboelectric, piezoelectric, and dielectric elastomer energy harvesters utilize distinct physical principles, such as the electrochemical double layer effect [23–26], triboelectrification effect [27,28], piezoelectric effect [29], and variable electrostatic capacitor principle [30], respectively, to harness mechanical energy

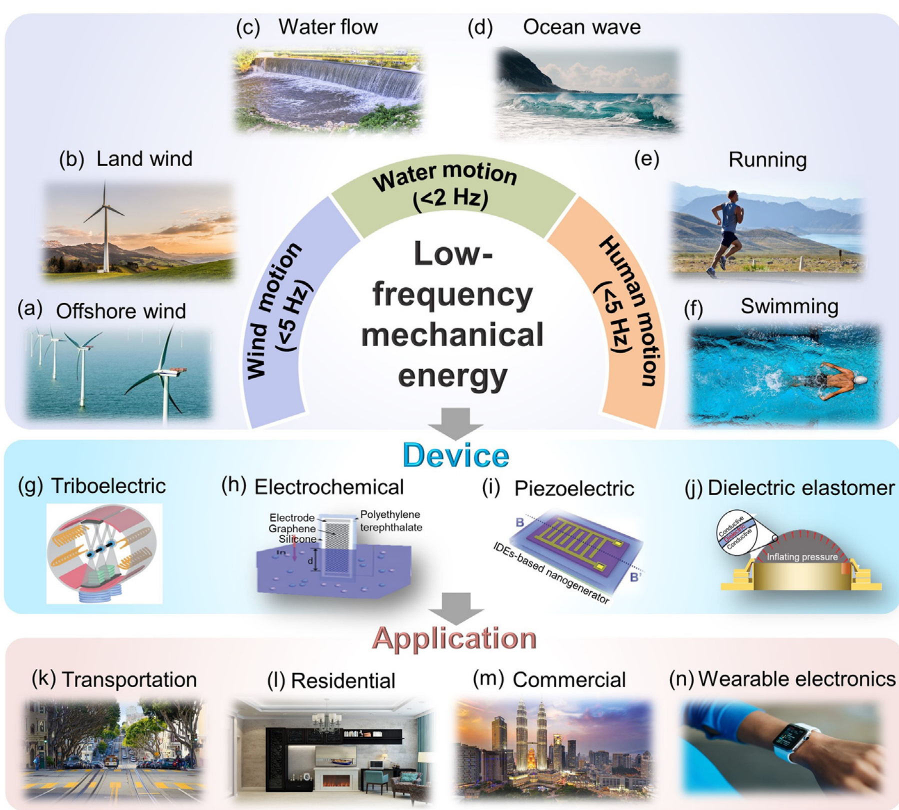


Fig. 1. (Color online) Overview of low-frequency mechanical energy harvesting and application demonstrations. (a) Offshore wind. (b) Land wind. (c) Water flow. (d) Ocean wave. (e) Human running. (f) Human swimming. (g) Triboelectric energy harvester. Reprinted with permission from Ref. [16], Copyright © 2021 Wiley. (h) Electrochemical energy harvester. Reprinted with permission from Ref. [17], Copyright © 2014 Springer Nature. (i) Piezoelectric energy harvester. Reprinted with permission from Ref. [18], Copyright © 2014 Wiley. (j) Dielectric elastomer energy harvester. Reprinted with permission from Ref. [19], Copyright © 2017 MDPI. Application for (k) transportation, (l) residential, (m) commercial and (n) wearable electronics.

(Fig. 1g–j). Unlike electromagnetic energy harvesting, these methods do not rely on rotor motion and can be designed with a diverse range of materials to enable better low-frequency operation while maintaining advantageous properties, such as light weight and small size. Due to the growth potential in technology, such as materials and design, we focus our discussion on these four energy harvesting approaches, which have been extensively investigated and hold great promise for a wide range of applications in industrial production and daily life (Fig. 1k–n).

While triboelectric, electrochemical, piezoelectric, and dielectric elastomer energy harvesting methods offer advantages over electromagnetic energy harvesting for low-frequency mechanical energy harvesting, they do have their limitations, including low output power, current, and energy conversion efficiency under low-frequency mechanical actions. In addition, the electrochemical energy harvesters have the limitation of low voltage. To address these challenges, researchers are exploring innovative techniques through structural design optimization, advanced materials development, and the incorporation of new energy conversion mechanisms to improve energy conversion efficiency under low-frequency mechanical actions [31–34]. These efforts are crucial for realizing the full potential of these energy harvesting methods for practical applications in various fields. In addition, environmental changes, such as humidity and temperature, can also impact the output performances of low-frequency energy harvesters [35,36]. This review explores the challenges of low-frequency energy harvesting and the key factors that influence the performance of mechanical energy harvesters, including their working mechanisms, environmental conditions, and device compositions. It aims to provide a comprehensive comparison and summary of the advantages and disadvantages of the different mechanisms suitable for low-frequency operation and presents strategies for enhancing their performance by modulating material compositions, structures, and devices. The review also examines the applications of mechanical energy harvesters in harvesting energy from waves, wind, and human motions, and offers recommendations for selecting appropriate mechanical energy harvesters with specific mechanisms for various applications to guide their design and fabrication. This analysis provides valuable insights into the critical factors and strategies for improving the efficiency of low-frequency energy harvesting technologies.

2. Critical aspects affecting the low-frequency performance of mechanical energy harvesters

Triboelectric, electrochemical, piezoelectric and dielectric elastomer energy harvesting are promising methods for low-frequency energy harvesting due to their unique advantages. However, the performance of these methods is also affected by device compositions and environmental factors, which can limit their low-frequency output. In this context, we introduce these four energy harvesting methods and analyze their working mechanisms, the impact of device compositions and environmental factors, and strategies to improve their output performance under low frequencies.

2.1. Critical aspects affecting the low-frequency performance of triboelectric energy harvesters

2.1.1. Working mechanisms of triboelectric energy harvesters

Triboelectrification is a process of charges being generated on the surfaces of two different materials when they come into contact or slide over each other, resulting in electron transfer between the two materials due to the interaction of their electron clouds (Fig. 2a) [37]. Professor Wang and his team [27] firstly proposed an innovative method of energy harvesting in 2012 named the "triboelectric nanogenerator (TENG)", which opened the exploration and utilization of triboelectrification. They developed various TENGs with different materials and structures which demonstrated a wide range of applications such as ambient energy harvesting and self-powered sensing techniques. The invention of the TENG has greatly promoted the development of energy harvesting and greatly expanded the approaches of development of energy harvesting from ubiquitous activities, such as human motions, waves and wind. In addition, they have made great advancement in function integration in recent years, indicating the direction for the future development of energy harvesting [9–11,14]. In order to unify the terminology, we have used the "harvester" throughout the article.

There are four operating modes for triboelectric energy harvesters: vertical contact-separation (CS) mode, lateral sliding (LS) mode, single-electrode (SE) mode, and freestanding triboelectric-layer (FT) mode [45]. The most commonly used operational mode is the CS mode, where positive and negative charges accumulate on the surfaces of two materials due to the triboelectrification effect when they come into contact. When the distance between the two materials increases after the applied force is removed, the potential difference induced between the upper and lower electrodes, drives electrons to flow between the electrodes through an external circuit, generating a current. This process can be repeated by applying/removing the external force, allowing for the continuous generation of electrical output (Fig. 2b) [38].

The amount of charge that accumulates during the contact process between two materials eventually reaches a saturation value, which is governed by the properties of the materials. This saturation value increases as the difference in triboelectric polarity of the two materials increases, and repeated contact between them is necessary to achieve this [29]. As such, as the external force frequency increases, the contact speed also increases. This leads to more electrons being transferred per unit time, resulting in continuous accumulation of charge. In addition, the device reaches saturation in a shorter time. The frequency of the external forces affects both the rate of charge transfer and the saturation charge density. Theoretical reports have showed that the output voltage generated by a triboelectric energy harvester can be expressed as $V = Q/C = \sigma x/\varepsilon_0$, where ε_0 is the permittivity of vacuum, x is the displacement, and σ is the triboelectric surface charge density [46]. Once the charge density reaches saturation, the output voltage becomes independent of the frequency. A higher frequency of the external force results in a faster charge transfer rate and a higher output current per time under the same conditions [20].

Triboelectrification is a well-known phenomenon that occurs in most materials, including metals, polymers, wood, glass, etc. This makes it possible to choose from a wide range of materials for triboelectric energy harvesting [47]. The greater the difference in triboelectric polarity between two materials, the more electrons gained or lost, the better performance of the triboelectric energy harvester under low frequencies. Polytetrafluoroethylene (PTFE) is a commonly used negative triboelectric material due to its higher electron-gaining ability, while aluminum (Al) and copper (Cu) are commonly used positive triboelectric materials due to their higher electron-losing ability and good conductivity.

2.1.2. Effect of device designs on triboelectric energy harvesters

Triboelectric energy harvesters are composed differently based on their working modes, which are suitable for low-frequency scenarios. Typically, CS mode triboelectric energy harvesters consist of positive and negative triboelectric materials, metal electrodes, and an external circuit. These materials are arranged face-to-face, with electrodes attached, and move perpendicularly to the friction interface. CS mode harvesters are often used for wave and human

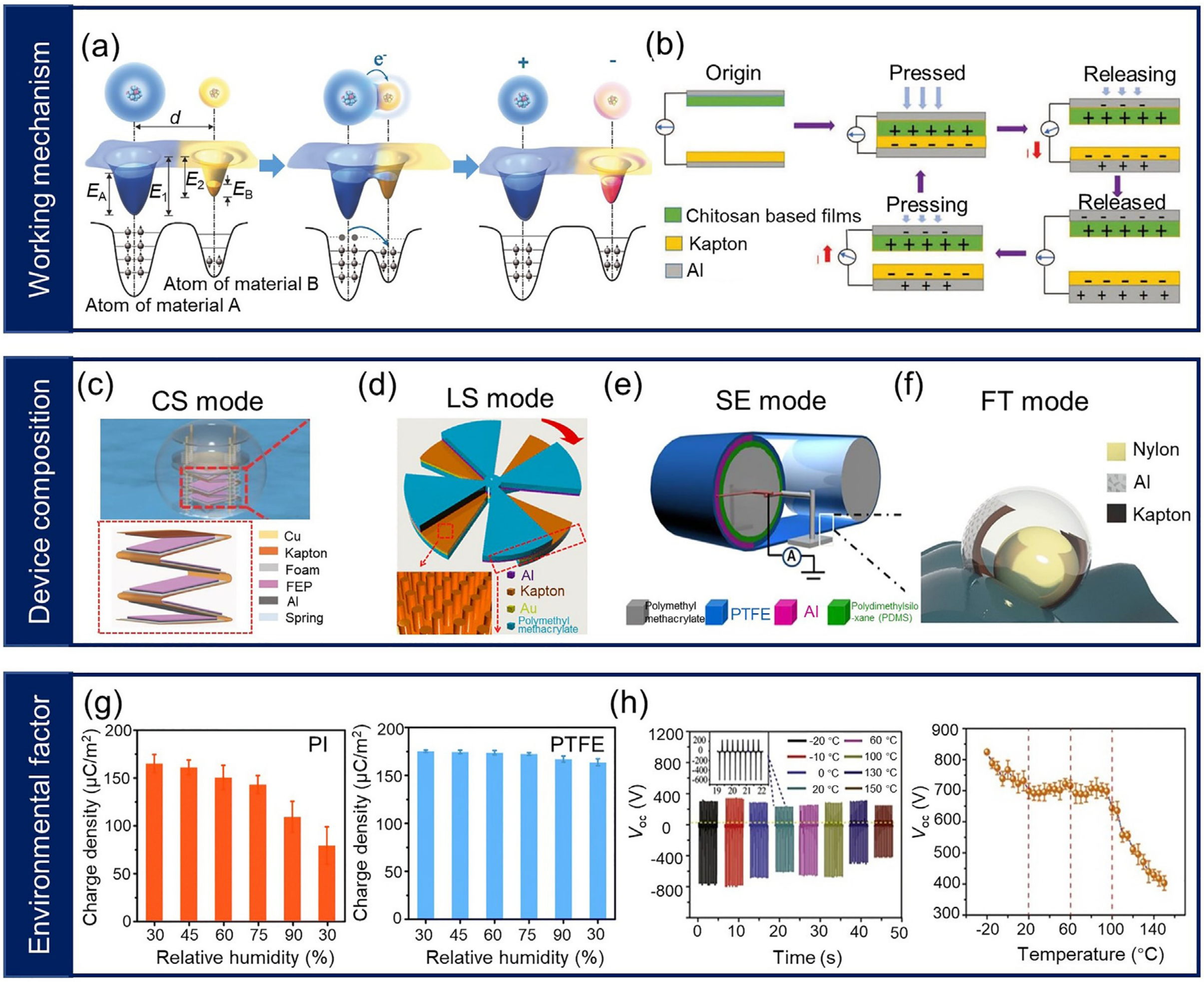


Fig. 2. (Color online) Critical aspects affecting the performance of triboelectric energy harvesters. (a) Schematic diagram of an electron-cloud-potential model. Reprinted with permission from Ref. [37], Copyright © 2018 Wiley. (b) Schematic diagram of working mechanism of triboelectric energy harvester. Reprinted with permission from Ref. [38], Copyright © 2018 Wiley. (c) CS mode harvester. Reprinted with permission from Ref. [39], Copyright © 2018 Wiley. (d) LS mode harvester. Reprinted with permission from Ref. [40], Copyright © 2013 American Chemical Society. (e) SE mode harvester. Reprinted with permission from Ref. [41], Copyright © 2014 Elsevier. (f) FT mode harvester. Reprinted with permission from Ref. [42], Copyright © 2015 Wiley. (g) Effect of humidity on the charge density of PI (left) and PTFE (right). Reprinted with permission from Ref. [43], Copyright © 2021 The Royal Society of Chemistry. (h) Effect of temperature on the voltage of triboelectric energy harvester. Reprinted with permission from Ref. [44], Copyright © 2017 Wiley.

walking energy harvesting and can be designed with a spring-assisted structure to convert low-frequency motion into high-frequency motion to improve energy harvesting efficiency [39,48–52]. The composition of the harvester varies depending on the application scenarios. For example, a spherical triboelectric energy harvester can be designed for wave energy harvesting with a spring-assisted multilayer structure. The multilayer structure comprises fluorinated ethylene propylene (FEP) as the negative triboelectric layer, Al foil as both positive triboelectric material and electrode, Kapton film, and foam (Fig. 2c) [39]. A seesaw structure can increase the contact speed between positive and negative triboelectric materials [48], while the oscillating structure can improve space utilization [51]. Additionally, the butterfly component design can enable wave energy harvesting in multiple directions [52].

The LS mode is similar to the CS mode, but the triboelectric material moves parallel to the friction interface. A disk [40] or cylindrical [53] structure can be used in the LS mode to convert water flow or wind force into rotational motion, which generates electrical energy (Fig. 2d). The LS mode provides higher output performance than the CS mode, but it is less durable because the material is susceptible to mechanical abrasion. The SE mode requires only one triboelectric material and one electrode, and the moving object can be used as the second triboelectric material. For example, a rotating wheel with PTFE as the triboelectric material and Al as the electrode can be used to harvest energy from the rotating motion (Fig. 2e) [41]. Finally, the FT mode typically uses a moving triboelectric material and a non-moving electrode and can be designed as a rolling structure [42,54,55]. For instance, a rolling harvester made of nylon balls enclosed in a spherical shell with fixed Al electrodes on the inner wall can generate voltage from wave motion (Fig. 2f) [42]. The duck-shaped structure is another design of the FT mode, which can convert wave motion into the pitching motion of the harvester and drive the rolling of the nylon balls to generate electricity [56].

2.1.3. Environmental factors on the performance of triboelectric energy harvesters

The performance of a triboelectric energy harvester is directly related to the generation and accumulation of charges. Therefore, any environmental factors that can affect this process would have an impact on the output performance. High humidity can have a negative effect on the performance of triboelectric energy harvesters in certain application scenarios, such as those involving oceans or rivers. Creation of a water film from humidity adsorption to the hydrophilic triboelectric surfaces obstructs direct contact between the two materials and diminishes charge generation. Moreover, the water film increases the conductivity of the friction interface, leading to charge transfer and neutralization. Airborne water molecules can also accelerate the dissipation of surface charges [35]. Studies have shown that the performance of triboelectric energy harvesters in solid–solid contact mode generally declines as humidity level rises [36,43,57,58]. For instance, when testing the charge levels of triboelectric energy harvesters made of polyimide (PI) and PTFE films at various humidity levels, the surface charge density of the PI film device decreased from 165 to 109 $\mu C/m^2$ as relative humidity increased from 30% to 90%. Similarly, the surface charge density of the PTFE film device decreased from 175 to 167 $\mu C/m^2$. Additionally, the effect of humidity on performance is irreversible, as the surface charge of the materials cannot return to its initial value even when the relative humidity returns to 30% (Fig. 2g) [43]. It is a common trend that the output performance decreases with the increase of humidity, but other studies have different views about the effect of humidity on performance [59–62]. For example, the current of a cyanoethyl cellulose-PTFE based TENG increased from 8.6 to 42 μA when the humidity was increased from 15% to 95% relative humidity [59]. In addition, some humidity-resistant harvesters have been developed in recent years, which can maintain their performance under varying humidity conditions [61].

Temperature changes can also affect the performance of triboelectric energy harvesters when exposed to direct sunlight or installed in highland areas. During the triboelectrification process, increased temperature leads to fluctuating and unstable electron energy, causing electrons to either return to the original material or be emitted into the air, thereby reducing charge accumulation [37]. On the other hand, increased temperature can also soften polymers such as PTFE, and the softened surface is easy to deform, increasing the contact area between the materials, facilitating charge transfer, and enhancing output performance. Nevertheless, excessive temperatures can damage the material and result in a loss of performance [63]. For example, when testing a harvester with PTFE and Al at different temperatures, the output voltage gradually decreased as the temperature increased from −20 to 20 °C. As the temperature rose from 20 to 60 °C, the output voltage showed a small increase. However, when the temperature continued to rise above 100 °C, the output voltage decreased rapidly (Fig. 2h) [44]. This example highlights the importance in considering the effects of temperature changes when designing and implementing triboelectric energy harvesters for practical applications.

In addition, the environmental atmosphere also has an influence on performance [64,65]. This is because different gases have different dielectric strength and breakdown voltages. For example, the output performances of the enclosed cubic triboelectric energy harvesters filled with N_2, CO_2, CHF_2Cl, and SF_6 gases were better than that filled with air. In addition, the highest voltage of 500 V was obtained in the SF_6 atmosphere, which increased 67% than that of filled with air [64].

2.2. Critical aspects affecting the low-frequency performance of electrochemical energy harvesters

2.2.1. Working mechanisms of electrochemical energy harvesters

While carbon nanotubes (CNTs) were first found to be able to generate power in fluids, the phonon towing model, the electrochemical double layer model, and the electric friction model were proposed, collectively referred to as electrochemical energy harvesting mechanism. The phonon towing model, proposed by Král and Shapiro [23], suggests that when fluids move on CNT surfaces, the resulting phonons tow free carriers in a direction that generates an electric current (Fig. 3a). The electrochemical double layer model reveals that when nanocarbon materials such as CNTs [24] and graphene [17] deform in ionic electrolytes, like aqueous NaCl or HCl, changes occur to the electrochemically available surface area, where charges can be adsorbed on the electrode material (Fig. 3b). These changes affect the electrochemical potential, which, in turn, fluctuates due to the variation in electrochemical double layer capacitance. In accordance with the equation, $I = Qf$, the output current is dependent on the pressure-induced charge change per cycle (Q) and the frequency (f). The electric friction model, proposed by Persson et al. [26], suggests that when a solution flows across the CNT surface, the ions in the solution are adsorbed onto the CNT surface and desorb after sliding for a distance due to solution flow. Carriers inside the material follow the movement, thereby generating electrical signals inside the CNTs. Overall, these mechanisms are based on the electrochemical double layer effect of nanomaterials formed in ionic solutions. Through changing the interaction between fluids and materials, electrical signals can be generated due to the change of electrochemical double layer state.

When selecting electrode materials for an electrochemical energy harvester, it is crucial to consider factors such as electrical conductivity, corrosion resistance, and structural stability. Metal electrodes are prone to corrosion in electrolytic environments, while polymeric materials have poor conductivity, making them unsuitable for this application. Nanocarbon materials, such as CNTs [24,25,66–70] and graphene [17,69,71], represent a better choice for electrodes due to their high specific surface area for ion adsorption, good structural stability and corrosion resistance, allowing for long-term operation in electrolytic environments like oceans and human tissue fluids. Additionally, they are highly adaptable for various structural designs, such as yarn-like [24,66,69] or film-like [17,67] structures, which exhibit excellent mechanical strength and flexibility. This makes them effective for harvesting low-frequency environmental energy like waves and human movement.

2.2.2. Effect of device designs on electrochemical energy harvesters

An electrochemical energy harvester typically consists of a working electrode, an electrolyte, and an external circuit, while some structures may also include a counter electrode. The working electrode converts mechanical energy into electrical energy by generating deformation. The electrolyte provides ions, and the external circuit stores the collected energy. The counter electrode, if present, generates a potential difference with the working electrode and serves as a reference potential.

Electrochemical energy harvesters are designed in accordance with their intended low-frequency scenarios. For example, for human-motion scenarios, the energy harvesters should be stretchable (Fig. 3c), making fiber and yarn electrodes a good choice due to their ability to deform up to 70% [66,72] or 100% [70]. Artificial muscles made of CNT fiber can also be used because they are stretchable and can conform well to human skin [73,74]. For ocean wave scenarios, energy harvesters should be compressible, making foam [71] and film [67] electrodes a good choice. Wave energy harvesters can be designed using CNT films, carbon films, and ceramic plates (Fig. 3d) [67], or by tying fiber electrodes to balloons (Fig. 3e) [24]. Additionally, while a single CNT can be used, in principle, for energy harvesting based on phonon towing (Fig. 3f) [68], this method is not widely studied.

2.2.3. Environmental factors on the performance of electrochemical energy harvesters

The output voltage of an electrochemical energy harvester is closely linked to several factors, including the number of ions adsorbed on the working electrode, the ease of adsorption and

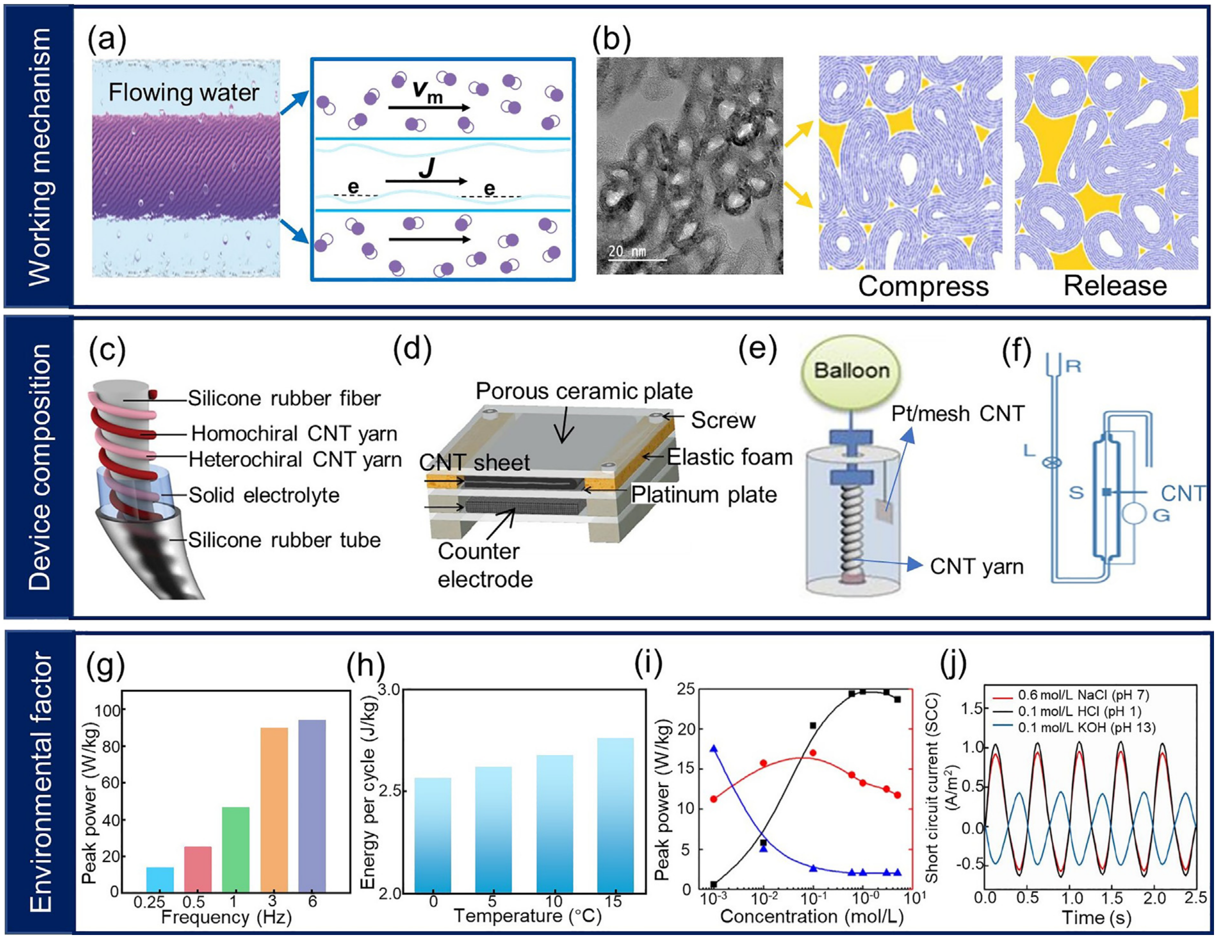


Fig. 3. (Color online) Critical aspects affecting the performance of electrochemical energy harvesters. (a) Schematic diagram of phonon towing model. Reprinted with permission from Ref. [23], Copyright © 2000 The American Physical Society. Reprinted with permission from Ref. [25], Copyright © 2017 Wiley. (b) Schematic diagram of electrochemical double layer model. Reprinted with permission from Ref. [24], Copyright © 2017 American Association for the Advancement of Science. (c) A wearable device. Reprinted with permission from Ref. [66], Copyright © 2020 Wiley. (d) A CNT film device. Reprinted with permission from Ref. [67], Copyright © 2020 Wiley. (e) A CNT yarn device. Reprinted with permission from Ref. [24], Copyright © 2017 American Association for the Advancement of Science. (f) A CNT device based on phonon towing model. Reprinted with permission from Ref. [68], Copyright © 2003 American Association for the Advancement of Science. Effect of (g) frequency and (h) temperature on the performance of CNT yarn harvester in 0.6 mol/L NaCl electrolyte. (i) Effect of NaCl solution concentration on the performance of CNT yarn harvester at 1 Hz. Reprinted with permission from Ref. [24], Copyright © 2017 American Association for the Advancement of Science. (j) Effect of electrolyte type on the performance of a CNT film harvester. Reprinted with permission from Ref. [67], Copyright © 2020 Wiley.

desorption, and the rate of ion migration. Any changes in these conditions caused by environmental factors can affect the efficiency of the energy harvesting process. Higher frequencies result in shorter ion migration times in the electrode, reducing the electrochemically available surface area, potential, and energy conversion efficiency. Conversely, lower frequencies allow for longer ion migration times, resulting in a larger electrochemically available surface area, higher potential, and greater energy conversion efficiency. However, lower frequencies can also lead to lower output power since the output power is time-dependent (Fig. 3g) [24].

In addition to the frequency of mechanical motions, the performance of electrochemical energy harvesters can also be impacted by environmental factors such as temperature and salinity. For example, higher temperatures increase the thermal movement of ions, making it easier for them to detach from the working electrode and thus increasing energy conversion efficiency. A study has demonstrated that the energy per cycle of a CNT yarn energy harvester increased by approximately 8% from 2.56 to 2.76 J/kg when the temperature was raised from 0 to 15 °C (Fig. 3h) [24]. In another example, the peak power of an electrochemical energy harvester increased with increasing salinity from 0.001 to 5 mol/L, reaching a maximum of 24.7 W/kg at a salinity of 1 mol/L, and decreased beyond this value. At lower concentrations, the decrease in electrolyte conductivity resulted in a rise in load resistance, causing a drop in peak power. This results from the load resistance maximizing power output at these concentrations. On the other hand, the drop in peak power at higher concentrations is due to a decrease in the peak-to-peak open circuit voltage (OCV) (Fig. 3i) [24]. In addition, the type of electrolyte used in electrochemical energy harvesters, either acidic or alkaline, can also influences their performance. For instance, it was demonstrated that a CNT film electrochemical energy harvester exhibited twice the performance in a 0.1 mol/L HCl electrolyte compared to that in a 0.1 mol/L KOH electrolyte (Fig. 3j) [67]. This difference is attributed to more ions being absorbed on the CNT film in the HCl electrolyte.

2.3. Critical aspects affecting the low-frequency performance of piezoelectric energy harvesters

2.3.1. Working mechanisms of piezoelectric energy harvesters

In principle, piezoelectric energy harvesters operate by utilizing the voltage produced by a material when deformed or vibrated, known as the piezoelectric effect. In a piezoelectric energy harvester, the applied force generates polarized charges at both ends of the material, resulting in electrostatic induction and the generation of induced charges at the two electrodes. This induced potential difference drives the charge to flow between the upper and lower electrodes through an external circuit. When the force is removed, the piezoelectric material gradually recovers both mechanically and electrically, and the charge flows in the opposite direction [15]. By cyclically applying and withdrawing force, mechanical energy can be converted into electrical energy (Fig. 4a) [75]. The study of piezoelectric energy harvesting began with the exploration of electrical power generation through the application of external force to ZnO nanowires (Fig. 4b), where Wang and Song [8] firstly proposed "piezoelectric nanogenerator". Since that report, a variety of piezoelectric energy harvesters have been reported using piezoelectric ceramics [32,33] and polymers [34]. While the fundamental working mechanisms are all based on piezoelectric effect, there are some differences between these two types of materials. For piezoelectric ceramics, the crystal structure changes under the external force, resulting in the piezoelectric effect caused by the non-coincidence of positive and negative charges. For polymers, on the other hand, the molecular chains move under the external force [15].

The piezoelectric coefficient measures how well a material can convert mechanical energy into electrical energy. The higher the coefficient, the more efficient the conversion. The amount of energy produced by a piezoelectric energy harvester depends on how closely the frequency of the force matches the resonant frequency of the device. The resonant frequency is determined by the stiffness and density of material and is not affected by the initial motion. If the frequency of the external force is closer to the resonant frequency, the piezoelectric material generates a higher potential difference, resulting in a better output performance. The voltage produced by the energy harvester is determined by the equation, $V = \frac{d_{ij}}{\varepsilon_r \varepsilon_0} \sigma_{ij} g_e$, where d_{ij} is the piezoelectric coefficient, ε_r is the relative dielectric constant, ε_0 is the permittivity, σ_{ij} is the applied stress, and g_e is the distance between the top and bottom electrodes.

To improve the energy conversion efficiency of piezoelectric energy harvesters in low-frequency scenarios, the selection of piezoelectric materials with lower natural frequencies is important. This ensures that the frequency of the piezoelectric materials closely matches the frequencies of the external forces in low-frequency scenarios, i.e., "frequency matching". In addition, the piezoelectric coefficient of the piezoelectric material should also be considered. The natural frequency of piezoelectric ceramics can reach several thousand Hz or higher [78], making them

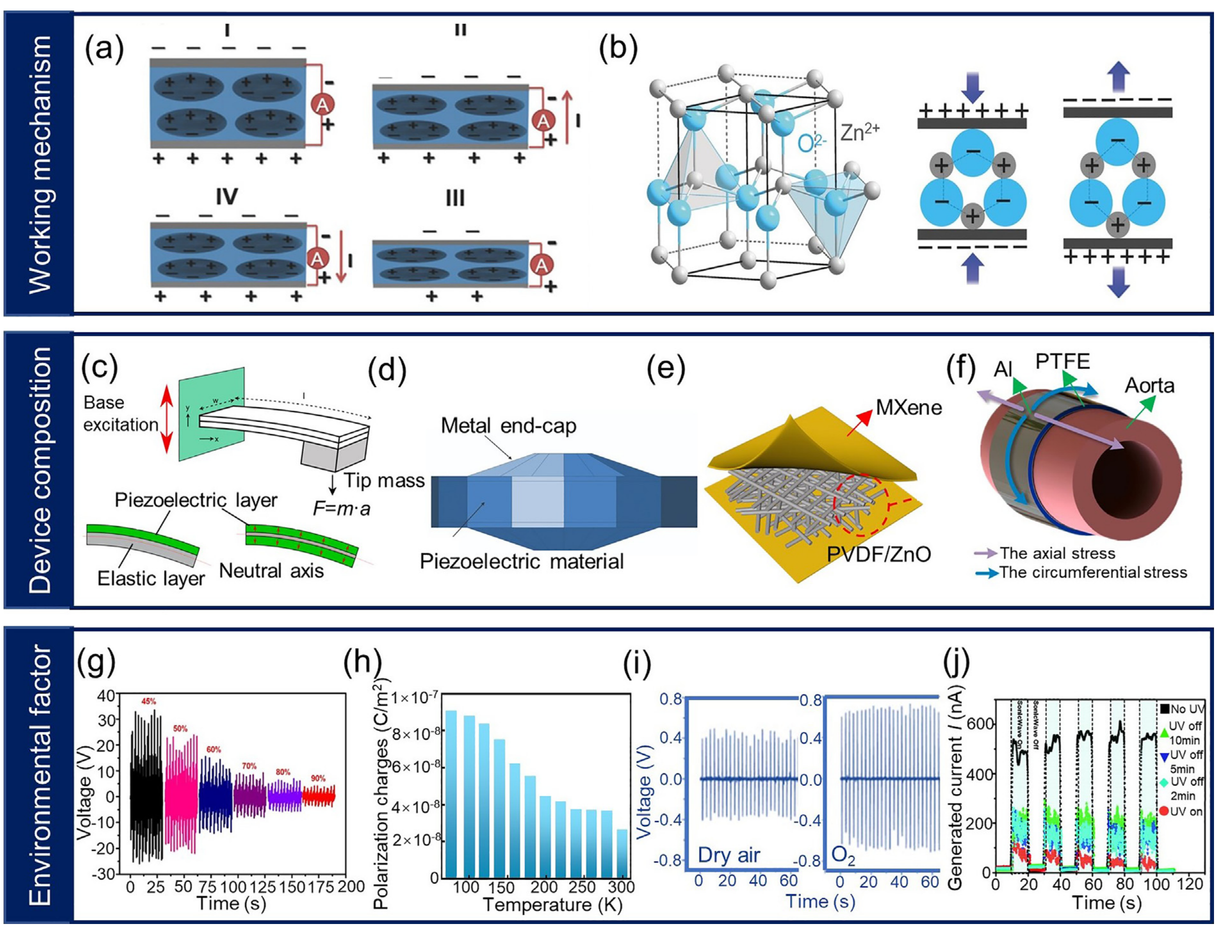


Fig. 4. (Color online) Critical aspects affecting the performance of piezoelectric energy harvesters. (a) Schematic diagram of working mechanism of piezoelectric energy harvester. Reprinted with permission from Ref. [75], Copyright © 2015 Wiley. (b) Schematic diagram of fundamental principle behind the piezoelectric effect. Reprinted with permission from Ref. [76], Copyright © 2016 Wiley. (c) A piezoelectric cantilever. Reprinted with permission from Ref. [77], Copyright © 2020 Elsevier. (d) A cymbal transducer. Reprinted with permission from Ref. [78], Copyright © 2014 AIP Publishing. (e) A flexible harvester. Reprinted with permission from Ref. [79], Copyright © 2018 Elsevier. (f) A film harvester. Reprinted with permission from Ref. [80], Copyright © 2016 Elsevier. (g) Effect of humidity on the voltage of a self-powered piezoelectric device. Reprinted with permission from Ref. [81], Copyright © 2018 American Chemical Society. (h) Effect of temperature on the effective polarization charges of ZnO nanowire. Reprinted with permission from Ref. [82], Copyright © 2013 American Chemical Society. (i) Voltage of ZnO piezoelectric energy harvester in dry air and O_2. Reprinted with permission from Ref. [83], Copyright © 2013 IOP Publishing. (j) Current of ZnO-nanowire based harvester under different illumination conditions of ultraviolet (UV) light. Reprinted with permission from Ref. [84], Copyright © 2008 American Chemical Society.

unsuitable for low-frequency mechanical energy harvesting from the perspective of frequency matching. However, the piezoelectric coefficient of piezoelectric ceramics is as high as 800 pC/N, which is much larger than that of piezoelectric polymer. Therefore, when selecting piezoelectric materials for energy harvesting, both the piezoelectric coefficient and the natural frequency represent critical elements to ensure optimal performance.

2.3.2. Effect of device designs on piezoelectric energy harvesters

A piezoelectric energy harvester typically consists of a piezoelectric material, an upper electrode, a lower electrode, and an external circuit. When the piezoelectric material is subjected to mechanical stress, it undergoes deformation, which generates an electrical charge. The charge transfer occurs between the upper and lower electrodes through the external circuit, resulting in the conversion of mechanical energy into electrical energy.

Various structures of piezoelectric energy harvesters have been developed based on this basic working mechanism and composition. Among them, the cantilever beam and cymbal structures are commonly used (Fig. 4c) [77]. The cantilever beam can generate a large mechanical strain during vibration and can be classified into unimorph or bimorph structures with a single layer or double ones of piezoelectric material, respectively. By incorporating a mass proof, the natural frequency of the device can be adjusted to improve the performance of the energy harvester. The cymbal structure is suitable for energy harvesting under high load conditions and consists of two metal cymbal-shaped end caps with a piezoelectric disk placed between them (Fig. 4d) [78]. Additionally, flexible thin film structures have been developed for piezoelectric energy harvesters [79,80,85], particularly for application scenarios, such as human motion and human–computer interaction. These structures usually consist of flexible piezoelectric and electrode materials. For instance, a self-powered piezoelectric sensor with a polyvinylidene fluoride (PVDF)/ZnO nanofiber film as the piezoelectric material and a flexible MXene electrode can be used for remote control of gestures in human–machine interactive system. The flexibility of these materials allows them to be attached to the robot's finger (Fig. 4e) [79]. Furthermore, a flexible film device composed of PTFE and Al film can be wrapped around the aorta to achieve self-powered blood pressure monitoring (Fig. 4f) [80].

2.3.3. Environmental factors on the performance of piezoelectric energy harvesters

The performance of piezoelectric energy harvesters can be affected by numerous environmental factors. One of these factors is humidity, especially in high humidity environments like those found in marine settings. Increased moisture adsorption on the piezoelectric material surfaces can lead to the neutralization or dissipation of the surface charge through electron or ionic conduction and ultimately result in degraded performance. For example, a voltage decrease from 30 to 4 V was observed as increasing relative humidity from 45% to 90% for a self-powered piezoelectric device (Fig. 4g) [81]. Similarly, a 33% drop in output voltage was found as relative humidity increased from 5% to 85% for a ZnO piezoelectric energy harvester [86].

Another environmental factor, temperature, can adversely impact the piezoelectric coefficient, with gradual decreases observed as temperature rises [82,87], resulting in a lower energy conversion efficiency and degraded performance. For instance, the charge density on the end face of ZnO nanowires dropped from 9×10^{-8} to 2.6×10^{-8} C/m^2 as temperature increased from 77 to 300 K (Fig. 4h) [82].

In addition to humidity and temperature, oxygen and radiation can also affect the performance of piezoelectric energy harvesters [83,84]. For example, pure oxygen environments can increase the voltage output of ZnO piezoelectric energy harvesters (0.7 V) compared to dry air environments (0.45 V) (Fig. 4i) [83]. Furthermore, sunlight exposure can negatively affect the performance of semiconductor-type piezoelectric materials, with current output dropping from 500 nA in the dark to 30–80 nA when exposed to UV radiation, as observed in a ZnO-nanowire based piezoelectric energy harvester (Fig. 4j) [84].

2.4. Critical aspects affecting the low-frequency performance of dielectric elastomer energy harvesters

2.4.1. Working mechanisms of dielectric elastomer energy harvesters

The concept of generating electrical energy through the deformation of acrylic has led to the study of dielectric elastomer energy harvesters. These harvesters rely on the deformation of a dielectric elastomer material when exposed to an external electric field [30]. Dielectric elastomers are elastic organic polymers with high dielectric properties and can undergo significant deformation. When subjected to an external electric field, the thickness of the material compresses due to electrostatic attraction while stretching in lateral direction. After the electric field is removed, the thickness of the material returns to its original state while the area decreases, maintaining volume invariance (Fig. 5a) [30].

Dielectric energy harvesters work based on the variable electrostatic capacitor principle, using a dielectric elastomer material to generate electrical energy through deformation. This process involves compressing the material to increase capacitance and stretching the bottom surface to convert mechanical energy into electrical energy. When an external force is applied, the thickness of the dielectric elastomer energy harvester decreases, causing an increase in capacitance from its lowest value ($C_{\min}$) to its maximum value ($C_{\max}$). An external power supply charges the device electrode, producing a voltage denoted by V_1. Upon removing the external force and power supply, the dielectric elastomer slowly returns to its original shape, which is characterized by a decrease in the capacitance and, in turn, generates another voltage, V_2. The charge on the electrodes is transferred through an external circuit, converting mechanical energy into electrical energy (Fig. 5b) [88]. The amount of energy harvested is determined by the difference between the output and input electrical energy (i.e., $½C_{\max}V_1^2$ and $½C_{\min}V_2^2$, respectively) when voltage is applied. The amount of energy generated depends on the level of deformation by the dielectric elastomer and the level of the applied external voltage. The efficiency of energy conversion is impacted by the frequency of stretching and contraction. The lower the frequency, the smaller the viscoelastic loss, and the higher the energy conversion efficiency.

According to the parallel plate capacitor model, using a material with high permittivity (i.e., the ability to store electric charge) can improve the output performance. Additionally, the material should also be able to repeatedly stretch and shrink during the energy harvesting process, and its capability to do so determines how efficiently energy can be harvested. Therefore, the material needs to be a good insulator and possesses excellent stretching properties, such as acrylic, silicone rubber, polyurethane (PU), and natural rubber.

2.4.2. Effect of device designs on dielectric elastomer energy harvesters

A dielectric elastomer energy harvester consists of two electrodes, a dielectric elastomer material sandwiched between the two electrodes and an external circuit. When the dielectric elastomer deforms, the capacitance of the device changes, which causes the electrodes to accumulate charge and then transfer it through the circuit. Thus, the material used for the device must be flexible enough to meet the deformation requirements.

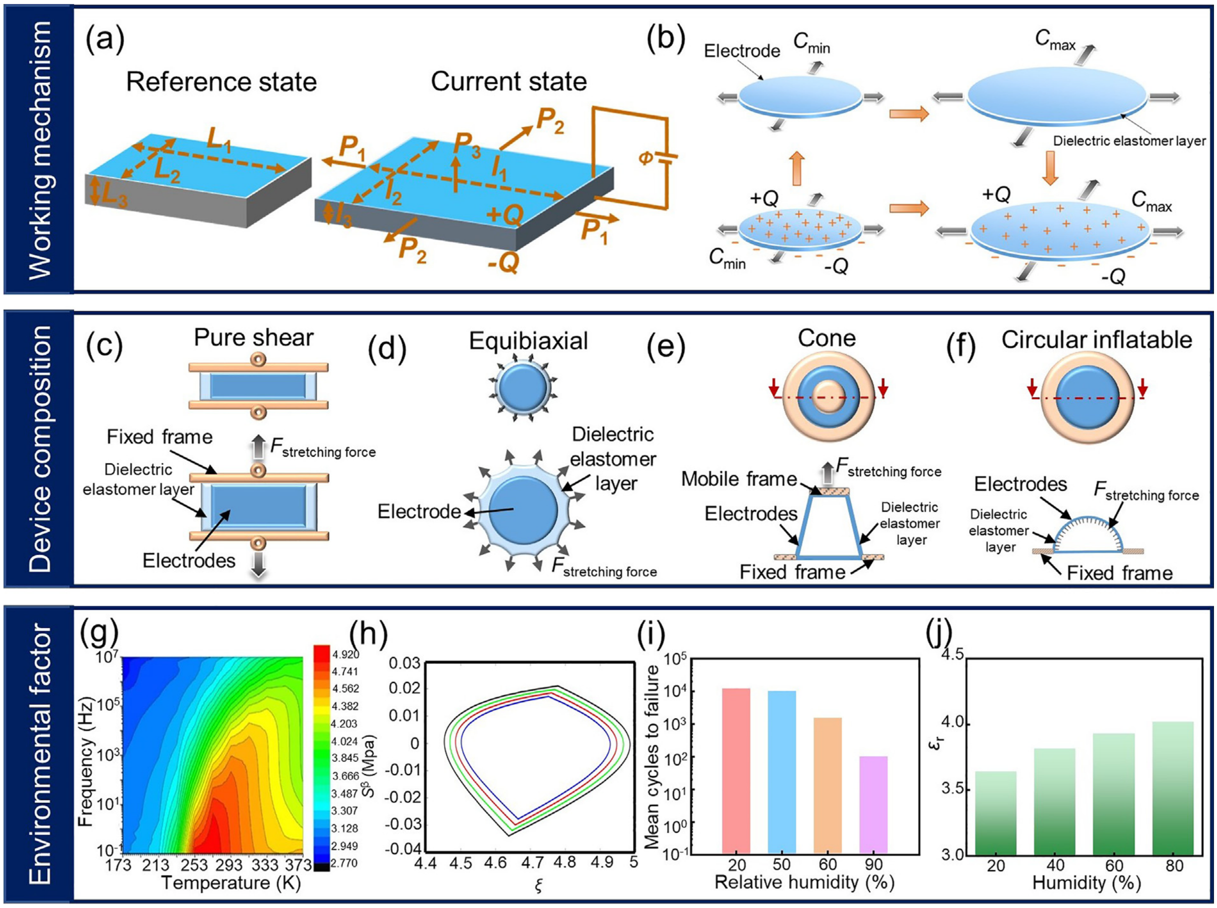


Fig. 5. (Color online) Critical aspects affecting the performance of dielectric elastomer energy harvesters. (a) Dielectric elastomer in the reference state and in the current state. Reprinted with permission from Ref. [30], Copyright © 2010 Elsevier. (b) Schematic diagram of the working cycle of a dielectric elastomer energy harvester. Reprinted with permission from Ref. [88], Copyright © 2020 Wiley. Schematic diagram of (c) a pure shear dielectric elastomer energy harvester, (d) an equiaxial dielectric elastomer energy harvester, (e) a cone dielectric energy harvester, and (f) a circular inflatable dielectric elastomer energy harvester. Reprinted with permission from Ref. [89], Copyright © 2021 MDPI. (g) Effect of temperature on the dielectric constant of acrylate. Reprinted with permission from Ref. [90], Copyright © 2012 Springer Nature. (h) Energy loss due to viscoelasticity at different temperatures (285 K (blue), 310 K (red), 335 K (green), and 360 K (black), from inside to outside). Reprinted with permission from Ref. [91], Copyright © 2016 IOP Publishing. (i) Effect of relative humidity on the mean time to failure of acrylate actuators. Reprinted with permission from Ref. [92], Copyright © 2013 Wiley. (j) Effect of humidity on the dielectric elastomer. Reprinted with permission from Ref. [93], Copyright © 2020 Elsevier.

The amount of electrical energy generated by the device depends on the degree of change in capacitance, which can vary based on the deformation mode and composition of the harvester. There are different modes of deformation, including uniaxial stretching, pure shear, equiaxial stretching, conical and circular inflation [89]. Uniaxial stretching involves longitudinal stretching and lateral shrinking, resulting in a small capacitance change. Under pure shear, the material is stretched longitudinally with little necking on the sides of the device, resulting in a relatively large capacitance change (Fig. 5c) [89]. Equiaxial stretching involves uniform stretching in each direction along the electrode plane, producing the maximum capacitance change for a given stretching force (Fig. 5d) [89]. However, this mode is more complex and requires connecting a set of pull wires along the perimeter of the dielectric film [94]. Conical and circular inflation modes involve out-of-plane deformation. Conical harvesters consist of a fixed frame, a conical diaphragm, and a mobile frame, and the capacitance changes as the mobile frame moves (Fig. 5e) [89]. Circular inflatable harvesters consist of a circular diaphragm and a fixed frame. The pressure difference between the inside and outside the diaphragm causes it to deform, resulting in a change in capacitance (Fig. 5f) [89]. This structure can be used for harvesting wave and wind energy [95,96].

2.4.3. Environmental factors on the performance of dielectric elastomer energy harvesters

Similar to triboelectric energy harvesters, the functionality of dielectric elastomer energy harvesters is also influenced by various environmental factors, such as temperature and humidity. Specifically, changes in temperature can impact the dielectric constant and energy loss of the device. For instance, the dielectric constant of acrylic varies with temperature, showing an initial increase followed by a decrease as the temperature rises from 173 to 373 K (Fig. 5g) [90]. This behavior is caused by the effect of increased molecule movement on the orientation polarization of the material. At low temperatures, it is challenging for the dipole to orient spontaneously, resulting in a low orientation polarization and hence a low dielectric constant. As the temperature increases, the ease of dipole orientation increases, causing the dielectric constant to increase as a function of temperature and reach a peak value at about 273 K at 1 Hz. However, as the temperature continues to increase, the thermal motion of molecular becomes more significant, causing them to become less aligned with each other. Therefore, the orientation polarization decreases, resulting in a decline in the dielectric constant.

In addition, temperature changes can impact the energy loss caused by the viscoelasticity of the material. When converting mechanical energy into electrical energy in dielectric elastomer energy harvesters, part of the energy is lost due to the viscoelasticity of the material, reducing the energy conversion efficiency. For example, one study has shown that the energy loss due to viscoelasticity increases as the temperature rises for the dielectric elastomer energy harvester (Fig. 5h) [91].

Humidity is another critical factor that affects the energy conversion efficiency and service life of dielectric energy harvesters [92,93,97]. Increased humidity results in more water molecules being absorbed by the dielectric elastomer energy harvester, which leads to charge loss that limits the cycling stability of the device [92]. For instance, one study reported that when the relative humidity increased from 20% to 90%, the cycle count of acrylate harvesters decreased by two orders of magnitude (Fig. 5i) [92]. In another study, the relative permittivity was found to gradually increase with increasing humidity (Fig. 5j) [93]. Thus, when utilizing dielectric elastomer energy harvesters in marine and river settings, accounting for the impact of humidity on device performance is essential.

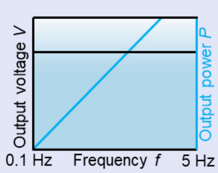
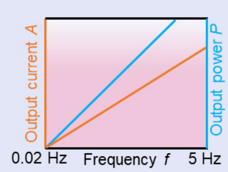
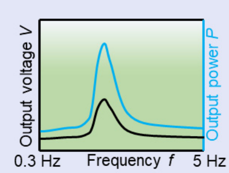
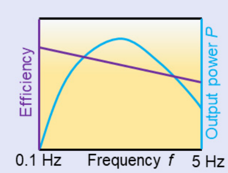
2.5. Summarization of critical aspects affecting the low-frequency performance of mechanical energy harvesters

Table 1 summarizes the performance-frequency dependence, device composition, and environmental effects of various energy harvesting methods by combining sections 2.1, 2.2, 2.3, and 2.4 and provides the following insights.

(1) The impact of frequency variation on the output performance of different types of energy harvesters differs. For triboelectric energy harvesters, the output voltage is related to the charge density, distance between two materials, and vacuum dielectric constant. The output voltage remains constant as the frequency decreases, while the current and power gradually decrease. For electrochemical energy harvesters, a lower frequency leads to more adequate electrode deformation and ion adsorption, resulting in higher output voltage but a gradual decrease in current and power. For piezoelectric energy harvesters, the maximum output performance is achieved when the mechanical frequency matches the resonant frequency of the device. For dielectric elastomer energy harvesters, reduced energy loss occurs at low frequencies, leading to an initial increase in output power as the frequency decreases. However, the output power gradually decreases as the frequency continues to decrease due to the corresponding increase in the period. Overall, these results show the different advantages and needs of each class of energy harvester. The low output performance at low frequencies is a significant challenge, primarily because the device can only generate output at frequencies similar to the input frequency, which limits its overall effectiveness.

(2) The basic components of the four energy harvesting methods differ based on their working mechanisms. Electrochemical

Table 1
(Color online) Summary of critical aspects affecting the low-frequency performance of mechanical energy harvesters.

		Triboelectric	Electrochemical	Piezoelectric	Dielectric elastomer
Calculation formula of voltage		$V=\frac{Q}{C}=\frac{\sigma x}{\varepsilon_0}$	$V=\frac{Q}{C}=\frac{\sigma S}{C}$	$V=\frac{d_{ij}}{\varepsilon_r\varepsilon_0}\sigma_{ij}g_e$	$V=\frac{C_{\max}V_1}{C_{\min}}$
Effect of frequency on performances					
Device compositions	Core material 1	PTFE, FEP, etc. [47–51]	Carbon nanomaterials [24,25, 66–71]	Ceramics, single crystals, polymers, etc. [32–34,77, 78]	Acrylic, natural rubber, PU, etc. [89,94–96]
	Core material 2	(Al, Cu, etc.) [50,51]	(Carbon nanomaterials, Pt mesh/CNT, etc.) [24, 66,67,69–71]	–	–
	Electrode 1	Al, Cu, etc. [47–51]	–	Al, Au, etc. [32–34,77,78]	Carbon black, CNT, metal, etc. [89,94–96]
	Electrode 2	Al, Cu, etc. [47–51]	–	Al, Au, etc. [32–34,77,78]	Carbon black, CNT, metal, etc. [89,94–96]
Deformation way		Contact, rub	Compress, stretch, twist	Compress, stretch	Compress, stretch
Environmental factors	Temperature	* −20 to 140 °C, voltage↓ [44]	0 to 15 °C, energy per cycle↑ [24]	77 to 300 K, charge density↓ [82]	285 to 360 K, efficiency↓ [91]
	Relative humidity	30% to 90%, voltage↓ [43]	–	5% to 85%, voltage↓ [86]	20% to 90%, cycle↓ [92]
	Salinity	–	10^{-3} to 1 mol/L, peak power↑ [24]	–	–

There are different trends about the effect of environmental factor on the performance of harvester, and we only describe the main trends found in most publications here.

energy harvesters include working electrodes made of nanocarbon materials and counter electrodes made of nanocarbon nanomaterials, Pt mesh/CNT, etc. Some devices may contain only working electrodes. Triboelectric energy harvesters rely on the triboelectrification between two materials and usually consist of negative triboelectric materials (such as PTFE, FEP, etc.) and their electrodes (made of Al, Cu, etc.), positive triboelectric materials (such as silk, woven, Al, Cu, etc.) and their electrodes (made of Al, Cu, etc.). Sometimes, metals like Al and Cu can serve as both positive triboelectric materials and electrodes. Piezoelectric energy harvesters consist of a piezoelectric material (such as ceramics, single crystals, polymers, etc.) and electrodes (made of Al, Au, etc.) at both ends of the material. Dielectric elastomer energy harvesters have dielectric elastomer materials (such as acrylic, natural rubber, PU, etc.) and electrodes on both ends of the materials (made of carbon black, CNT, metal, etc.). The working principle and basic composition of each device determine how it is subjected to forces, which affects its energy harvesting efficiency. Due to the particularity of the materials used, electrochemical energy harvesters have various deformation methods, including compression, stretching, twisting and loosening.

(3) Environmental factors also impact energy harvesting performances. Being aware of these effects can aid in the appropriate selection and packaging design to minimize negative effects. For instance, the voltage of triboelectric and piezoelectric energy harvesters decreases as humidity increases, whereas electrochemical energy harvesters need to operate in an electrolyte environment that is not affected by humidity. In scenarios such as marine and river applications, packaging design for triboelectric and piezoelectric energy harvesters is a crucial factor to consider. Although the output performance of electrochemical energy harvesters is affected by salinity, it is less affected within the range of 0.5 to 0.64 mol/L, and thus no additional packaging is needed. Additionally, the output voltage of both triboelectric and piezoelectric energy harvesters decreases with increasing temperature, whereas electrochemical energy harvesters benefit from higher temperatures. For dielectric elastomer energy harvesters, temperature increases can increase energy loss caused by viscoelasticity of the material, thereby reducing energy conversion efficiency, while humidity has an adverse impact on the cycle time of the device.

In summary, working mechanisms, device compositions, and environmental factors are critical aspects affecting the low-frequency performance of mechanical energy harvesters. The working mechanisms determine the frequency dependence of their output performance and understanding the mechanisms of various energy harvesting methods can improve the low-frequency output performance from the aspects of materials and structures. The device composition of energy harvesters is also an important factor affecting the low-frequency performance and appropriate composition should be chosen for the specific low-frequency scenario. In addition, the negative effects of environmental factors such as temperature and humidity should be avoided in practical applications to ensure output performance of mechanical energy harvesters under low frequency.

3. Strategies for the low-frequency performance improvement of mechanical energy harvesters

Harvesting energy from low-frequency mechanical motions, such as those generated by waves, wind, and human movements, can be challenging due to their low amplitude, multi-directionality, and intermittent nature. Nevertheless, it is possible to enhance the performance of mechanical energy harvesters operating at low frequencies by choosing suitable materials, modulating the structure, and developing specialized devices that take these characteristics into account. This can result in higher output voltage, current, power, energy conversion efficiency, and other benefits.

3.1. Material selection for the low-frequency performance

Material selection involves choosing from diverse neat materials, preparing composite materials by doping, or chemically modifying the surface of the material without changing its micromorphology (such as introducing functional groups on the surface of the material) to improve the low-frequency output performance.

3.1.1. Material selection: triboelectric energy harvesters

As previously described, triboelectric energy harvesters operate by transferring charge between two surfaces through contact and separation, leading to a potential difference due to the difference in electron affinity. This phenomenon harnesses frictional force and converts it into electrical energy through the triboelectric effect. To maximize the electrical output from low-frequency mechanical input, materials with high surface charge density are preferred. Thus, selecting positive/negative triboelectric materials with large differences in electron gain/loss capabilities [98], surface functionalization [99], and doping [100–104] are essential strategies for improving device performance.

Several studies have explored the electron gain/loss capability of materials [98,105–108]. For example, Xu et al. [98] investigated the output of the harvester with multiple negative triboelectric materials, such as FEP, Kapton, and PTFE, using Cu as the positive triboelectric material (Fig. 6a). They found that the PTFE film generated the highest voltage output (60 V) of the three, owing to its high electron-gaining ability, as it is a material with a relatively strong electron gaining ability in the triboelectric series. Nowadays, materials like PTFE [106], PDMS [107], and FEP [39] are widely used as negative triboelectric materials in low-frequency systems, such as wave motions and human motions, for triboelectric energy harvesters. In terms of positive triboelectric materials, metals, such as Al [39] and Cu [106], are popular choices due to their low friction coefficients and good conductivities. Animal hides and skins, as well as braided fabrics, have exhibited a stronger electron losing ability than metals. However, they possess large coefficients of friction, making relative motion with a negative triboelectric material challenging at low frequencies. Therefore, they are not commonly used as positive triboelectric materials for low-frequency mechanical energy harvesters. Recently, high-wear polymers are being developed to be used as the positive triboelectric material [108].

While metals, such as Al and Cu, do possess advantageous tribological and electrical properties for energy harvesting, they have limited electron-losing ability. Surface functionalization has been used to modify the functional groups on the material surface to enhance electron gaining/losing ability. Introducing fluorine (–F) on negative triboelectric materials has been used to enhance the electron gaining ability, while introducing amine (–NH_2) on positive triboelectric materials enhances electron losing ability. For example, functionalizing a thin film of Au with –NH_2 increased surface charge density from 68 to 140 $\mu C/m^2$ and current density from 9 to 18.5 mA/m^2 at 2.5 Hz (Fig. 6b) [99].

Additionally, the dielectric constant of triboelectric materials can be increased through doping to further enhance the surface charge density after contact or friction. Potential dopants include $SrTiO_3$ nanoparticles (NPs) [100], $BaTiO_3$ NPs [101], graphite particles (GPs) [102] and molybdenum disulfide [104], etc. For example, the addition of $SrTiO_2$ NPs to PDMS demonstrated an optimal peak voltage of 305 V at 2.5 Hz for 10 vol% $SrTiO_2$ doping, compared to just 172 V for a pure PDMS film (Fig. 6c) [100]. Similarly, adding $BaTiO_3$ NPs to a poly(vinylidenefluoride-co-trifluoroethylene) (P

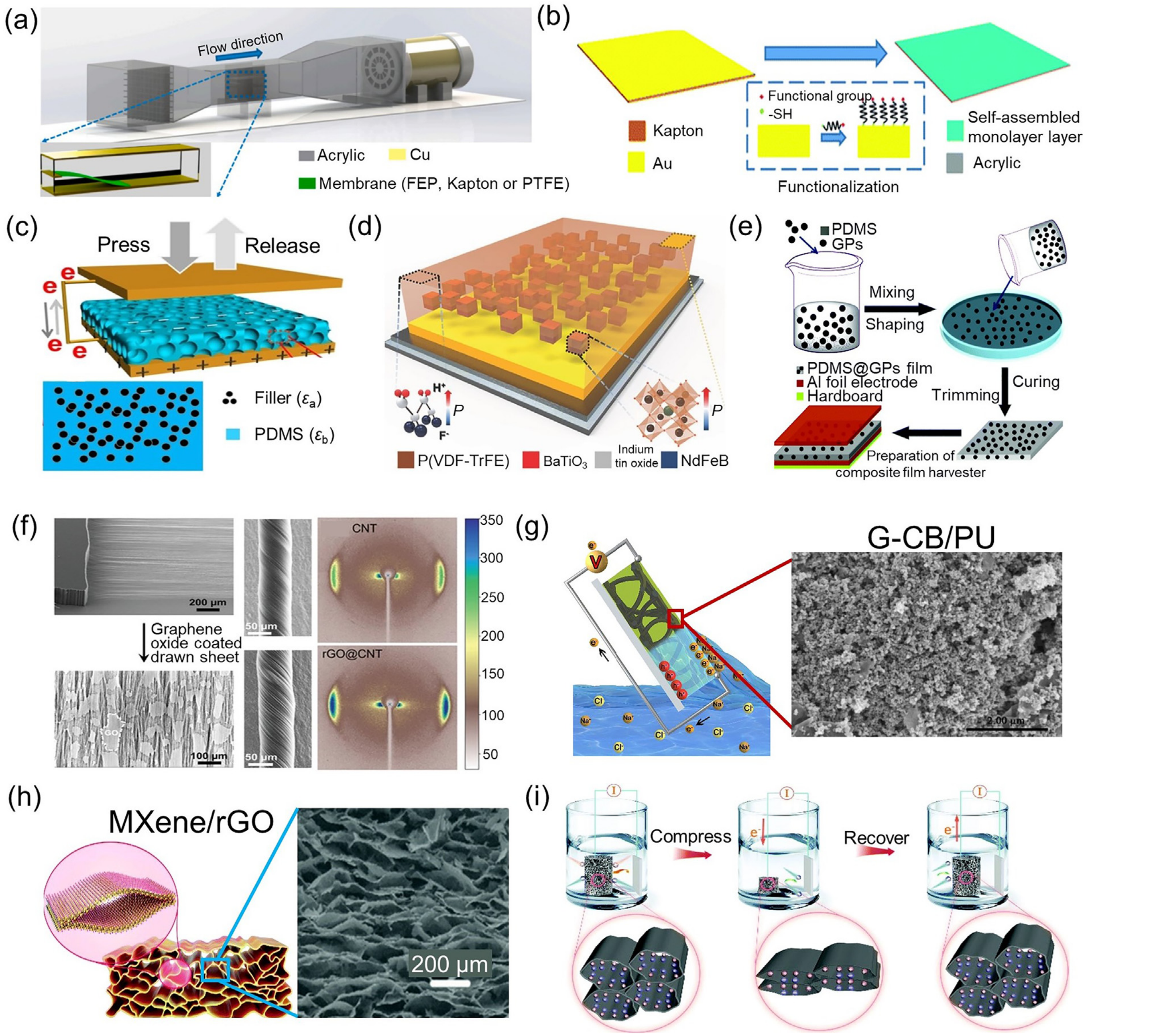


Fig. 6. (Color online) Material selection of triboelectric and electrochemical energy harvesters. (a) Material selection of a wind harvester. Reprinted with permission from Ref. [98], Copyright © 2017 Elsevier. (b) Process of functionalization of Au film. Reprinted with permission from Ref. [99], Copyright © 2016 The Royal Society of Chemistry. (c) Schematic diagram of a composite harvester. Reprinted with permission from Ref. [100], Copyright © 2015 American Chemical Society. (d) Schematic diagram of a ferroelectric composite-based harvester. Reprinted with permission from Ref. [101], Copyright © 2016 Wiley. (e) Schematic diagram of the process for fabricating the PDMS@GPs film. Reprinted with permission from Ref. [102], Copyright © 2015 The Royal Society of Chemistry. (f) SEM images and X-ray scattering patterns of CNT yarn and rGO@CNT yarn. Reprinted with permission from Ref. [69], Copyright © 2022 Wiley. (g) SEM image of 80 wt% G-CB/PU film. Reprinted with permission from Ref. [109], Copyright © 2018 Elsevier. (h) SEM image of the MXene/rGO aerogel. (i) Deformation of aerogel during compressing/recovering cycle. Reprinted with permission from Ref. [71], Copyright © 2021 The Royal Society of Chemistry.

(VDF-TrFE)) composite resulted in an output voltage of 330 V and a current of 0.26 mA, which were 2.6 and 5.5 times higher, respectively, than those of the triboelectric energy harvester with only a poled P(VDF-TrFE) (Fig. 6d) [101]. Finally, a triboelectric energy harvester using a PDMS and GP composite as negative triboelectric material and Al as positive triboelectric material showed a current output 4.5 times higher than that of the pure PDMS film at 2 Hz (Fig. 6e) [102].

Some new materials are developed for use in triboelectric energy harvesters, such as natural green materials [110–116] and aniline formaldehyde resin [117]. In particular, natural green materials, such as cellulose [111–114] and chitosan [115,116] have gained attention because of their biodegradability. For example, a cellulose organohydrogel based harvester can get the output of 205 V and 1.0 μA, which was higher or comparable to other hydrogel-based harvesters such as polyacrylamide-LiCl hydrogel [111]. In another example, the output voltage of cellulose II aerogel-based triboelectric energy harvester increased by 211% by blending cellulose and chitosan with a mass ratio of 2:1, compared to the pristine cellulose II aerogel-based triboelectric energy harvester under the same stress of 40 N. The improvement was found to originate from the electron-donating groups of chitosan to increase the surface charge density of the materials [116].

3.1.2. Material selection: electrochemical energy harvesters

In order to optimize the low-frequency performance of electrochemical energy harvesters, one strategy is to select materials that possess high charge adsorption capacity and electrical conductivity, while considering the electrochemical available surface area during the external force cycle. Nanocarbon materials [24,66–71,109], including CNTs [24,66–68,70], graphene [71], and nanocarbon-based composites [69,109], are the common choice in such applications. Of these, CNTs have emerged as a popular choice due to their strong charge adsorption capabilities, good conductivity, favorable mechanical properties, and ability to be fabricated into diverse shapes suitable for low-frequency motion. Consequently, CNTs exhibit potential for an array of energy harvesting applications, including the capture of mechanical energy from organ movements [70], as well as from wave [24] and wind [25] energies.

As a nanoscopic fibrous material, CNTs are well known to bundle when they come into contact with each other. This bundling reduces the available surface area for the electrochemical process, leading to decreased harvesting efficiency. To overcome this issue, researchers have employed combining this pseudo-one-dimensional (1D) material with materials of different dimensionality and composition. For example, Wang et al. [69] constructed a reduced graphene oxide@CNT (rGO@CNT) composite yarn as the working electrode for a yarn-based harvester (Fig. 6f) and demonstrated that this combination of materials greatly improved harvesting efficiency. The increased interactions between 1D nanotube bundles and two-dimensional (2D) nanosheets resulted in a dramatic improvement in voltage output from 325 to 380 mV, compared to pure CNT yarn, under 45% compressive strain at 1 Hz in 0.1 mol/L aqueous HCl.

In recent years, researchers have focused on adding other materials, such as carbon black [109] and MXene [71] to a nanocarbon matrix to enhance electrical conductivity and improve output performance. For instance, a film-type wave energy harvester was fabricated by casting a mixture of graphene and carbon black (G-CB) with waterborne PU on various substrates (e.g., glass, plastics) (Fig. 6g) [109]. The increase in output voltage of the device, from 0.7 to 11.14 mV, correlated directly with the G-CB content in the composites (from 30 wt% to 80 wt%). In another example, a 16.7 wt% MXene/rGO aerogel was developed for wave energy harvesting (Fig. 6h) [71]. Aerogels by combing MXene and rGO with better electrical conductivity were made into electrodes and exhibited a significant increase in voltage output from 35 to 150 mV under 10% compressive strain at 0.2 Hz compared to rGO aerogel alone (Fig. 6i). Moreover, this material showed reduced brittleness and improved deformability compared to the pure MXene aerogel, and could withstand 30% compressive strain with full recovery. The output voltage remained at about 92% of the initial voltage value even after 8000 cycles.

To summarize, the importance of the mechanical properties of the material cannot be overstated when it comes to ensure the long-term effectiveness of electrochemical energy harvesting. As such, nanocarbon materials are currently highly favored for use in such devices due to their advantageous electrical and mechanical properties.

3.1.3. Material selection: piezoelectric energy harvesters

Optimizing the performance of piezoelectric energy harvesters requires careful selection of materials based on two critical parameters: the piezoelectric coefficient and natural frequency. The resonant frequency of the harvester, which is strongly influenced by the natural frequency of the piezoelectric material, plays a significant role in determining its power output. Therefore, selecting piezoelectric materials with low natural frequencies is important to achieve frequency matching and maximize the performance. Additionally, the piezoelectric coefficient determines the amount of electrical charge generated in response to mechanical stress and further affects the output performance.

Commonly used piezoelectric materials include ceramics, polymers, and crystals, with ZnO and $BaTiO_3$ possessing low piezoelectric coefficients and $Pb(Zr_x, Ti_{1-x})O_3$ (PZT) and single crystals like $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PMN-PT) having high coefficients but also high elastic modulus and natural frequencies. One solution to this mismatch is fabricating high coefficient materials into thin sheets to enhance their response to low-frequency and low-amplitude mechanical effects [32,33,118]. For instance, a PMN-PT film-like harvester exhibited a 145 μA current at 0.3 Hz, which was 20 and 90 times higher than that of ZnO and $BaTiO_3$, respectively [33]. In another example, a flexible PZT film harvester generated a 200 V voltage and 35 μA current at 0.6 Hz, showcasing the potential of laser peeling methods [32].

From a frequency matching perspective, piezoelectric polymers are ideal for use in low-frequency environments due to their low natural frequency and good flexibility. However, their generally lower piezoelectric coefficients lead to inferior energy harvesting performance compared to piezoelectric ceramics and single crystals [119]. To address this issue, polymer-based composites incorporating ceramics or single crystals have been developed to increase piezoelectric coefficients while maintaining a lower natural frequency [120,121]. For example, $BaTiO_3$ NPs were added to P(VDF-TrFE) to fabricate a flexible piezoelectric energy harvester for human motion energy harvesting. The output voltage was found to increase with the mass fraction of $BaTiO_3$ NPs, resulting in a three-fold performance improvement at 0.35 Hz with a mass fraction of 40% compared to the case without $BaTiO_3$ NPs. These improvements were attributed to the high piezoelectric coefficient of $BaTiO_3$ [120].

3.1.4. Material selection: dielectric elastomer energy harvesters

The performance of dielectric elastomer energy harvesters relies on the capacitance changes of the material. This change can be maximized by selecting materials with a low modulus of elasticity, high dielectric constant, and low viscous loss. When the material undergoes deformation at low frequencies and amplitudes, those low-modulus materials can deform to a greater extent. Meanwhile, materials with a high dielectric constant can create significant capacitance changes during large deformations. Additionally, materials with low viscosity loss can enhance energy conversion efficiency by minimizing energy consumption through viscous loss during deformation.

Commonly used materials like acrylics and natural rubbers have limitations. For example, acrylics experience high viscosity loss during deformation and natural rubber possesses a high elastic modulus, which restricts deformation. To address these issues, developing composite materials that combine the advantages of different materials is an effective approach [122–124]. For example, adding $BaTiO_3$ NPs and dioctyl phthalate plasticizer to natural rubber resulted in a $BaTiO_3$/dioctyl phthalate/natural rubber composite with a low elastic modulus, high dielectric constant, and improved output performance. An output electrical energy density of 0.71 mJ/cm^3 and an energy conversion efficiency of 3.8% could be achieved, which was 3.8 and 4.7 times higher, respectively, than those of pure natural rubber [122].

Similarly, high energy density dielectric elastomer composites were achieved through the introduction of a low concentration of liquid acrylonitrile-butadiene rubber (LNBR) and TiO_2 into a silicone rubber matrix [125]. The improved dielectric constant was attributed to the strong dipole polarizability of LNBR and interfacial polarizability of LNBR@TiO_2. This composite achieved an impressive output electrical energy density of 62.1 mJ/cm^3.

Therefore, the development of composite materials that combine the desirable characteristics of different materials is a promising approach to overcoming the limitations of individual materials and improving the output performance of dielectric elastomer energy harvesters.

3.2. Structural modulation for the low-frequency performance improvement

Structural modulation refers to altering the micro-morphology (such as pyramidal or square microcolumn on the surface of the triboelectric material) and structural parameters (such as the diameter and height of the microcolumn) of the electromechanical conversion materials (such as the working electrodes in the electrochemical energy harvesters and the positive/negative triboelectric materials in the triboelectric energy harvester) to improve the low-frequency output performance.

3.2.1. Structural modulation: triboelectric energy harvesters

Triboelectric energy harvesters can have improved output performance by increasing the contact area between positive and negative triboelectric materials through changes to the surface morphology of the materials. This can be achieved by modifying the contact surfaces through patterning the surface with squares [126], pyramids [126], hemispheres [127], bowls [128], or making network structures [129] on the positive/negative triboelectric material. And the above surface morphology can be prepared by using methods like stencil [126], electrostatic spinning [129], etching [130], laser irradiation [131], or deposition [127]. For some polymer materials, the surface morphology can be modified using techniques like the template method or etching.

For example, patterned PDMS arrays with cubes or pyramids have been made using different depression features in silicon molds (Fig. 7a) [126]. When tested using polyethylene terephthalate (PET) as the positive triboelectric material, energy harvesters made of PDMS films with different surface morphologies showed different output voltages. The structured films with cubic or pyramidal features exhibited much higher output (16 and 18 V, respectively, at 0.33 Hz) than the unstructured film (3 V) due to their larger effective triboelectric effect generating more surface charges during friction (Fig. 7b). In another study, a concave hemisphere morphology was created on the surface of PDMS using ultrafast laser irradiation [131] (Fig. 7c). The performance of the harvester using laser-irradiated PDMS was found to exceed that of a bare PDMS (Fig. 7d). Regenerated silk fibroin films were also prepared using the electrospinning and casting methods (Fig. 7e) [129], with the same PI films used as the negative triboelectric material. The voltage output of the regenerated silk fibroin film obtained through the electrostatic spinning method was significantly higher (15 V at 1 Hz) than that prepared by the casting method (9 V) due to the entangled network of nanofibers formed from the spinning method (Fig. 7f).

In addition to modifying the surface morphology of polymers, altering the surface morphology of negative triboelectric metal materials, such as Al and Cu, is another approach. In the case of depositing Au NPs on Au films and PDMS, the increased contact area between the surfaces led to a 6.8-fold increase in current density and 5.09-fold increase in output voltage at 5 Hz than the same device without Au NP modification (Fig. 7g, h) [127]. In another

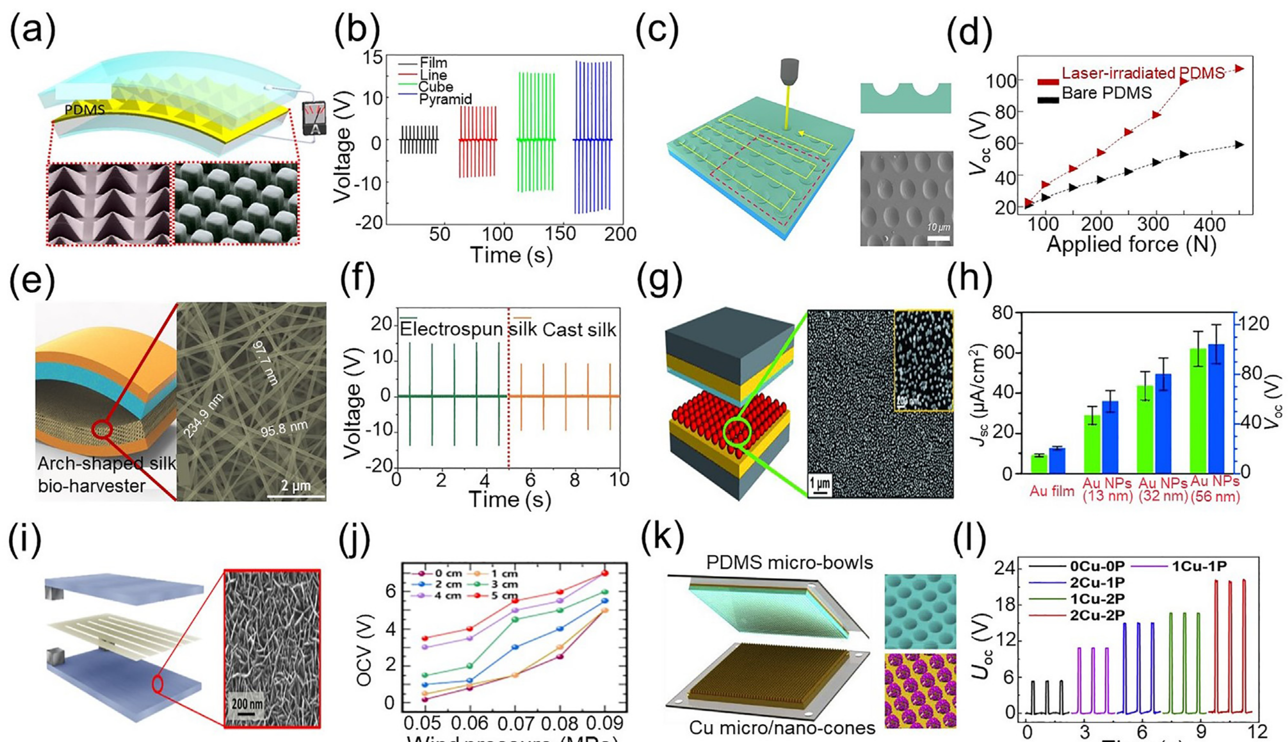


Fig. 7. (Color online) Structural modulation for the low-frequency performance improvement of triboelectric energy harvesters. (a) SEM image of the patterned PDMS thin film with cubic and pyramids features. (b) Output voltage of the harvesters using bare and various patterned PDMS thin films. Reprinted with permission from Ref. [126], Copyright © 2012 American Chemical Society. (c) SEM image of the laser irradiated PDMS at laser power of 29 mW. (d) Output voltage of the bare harvester and laser irradiated harvester as a function of the external force. Reprinted with permission from Ref. [131], Copyright © 2017 Elsevier. (e) SEM image of the electrospinning silk. (f) Output voltage of the harvesters using electrospinning silk and cast silk. Reprinted with permission from Ref. [129], Copyright © 2016 Wiley. (g) SEM image of the Au film modified with 56 nm Au NPs. (h) Output voltage and current density of different-sized Au NP-modified harvesters. Reprinted with permission from Ref. [127], Copyright © 2013 Wiley. (i) SEM image of the surface of Al electrode treated by water-assisted oxidation process. (j) Output voltage of harvesters under different weak winds. Reprinted with permission from Ref. [132], Copyright © 2020 MDPI. (k) Schematic diagram of Cu film with micro/nano structure and PDMS film with micro-bowls structure. (l) Output voltage of the harvesters with different micro/nano structures. Reprinted with permission from Ref. [128], Copyright © 2019 Elsevier.

study, with the nano-grass structure on the Al electrodes, the output voltage of the device was found to be 3.5 V higher than that without the such structure when subjected to 0.05 MPa wind pressure (Fig. 7i, j) [132].

Although changing the surface morphology of materials can increase contact area, the increase is limited at low-amplitude motions. To solve this problem and improve output performance, modifying the surface profile of both contact surfaces simultaneously is necessary. For example, using laser scanning ablation technology, micro/nano dual-scale structures were fabricated on Cu film surfaces in the form of cones, while micro-bowl structures were fabricated on PDMS surfaces using single pulse irradiation (Fig. 7k). The harvester with micro/nano-cones on the Cu film surface and micro-bowls on the PDMS surface produced a higher output voltage of 22 V at 1.5 Hz than the one without such structures (only 5 V) (Fig. 7l) [128].

3.2.2. Structural modulation: electrochemical energy harvesters

The strategy to enhance the low-frequency performance of electrochemical energy harvesters through structural modulation involves improving their structural ability to absorb multi-directional, low-frequency mechanical energies, which can change the amount of electrochemical available surface area under low-amplitude motion. Various material structures, such as yarns [24,66,69], flakes [67], sponges [71], fibrous [70] materials, lamellar structures, and other structural forms are currently utilized for low-frequency mechanical energy harvesting. For example, the lamellar structure, with its large force area, is well-suited for applications, such as absorbing wave lapping. To maximize the adsorption of mechanical input in a vertical direction while minimizing any interruption from the sides, a CNT sheet electrode with long intertube gaps was fabricated (Fig. 8a). The degree of alignment in the CNT sheets was increased by mechanically drawing a non-aligned sheet using a tensile stress up to 200 kPa. The resulting output voltage was found to be 1.6 and 2.4 mV at draw stresses of 100 and 200 kPa, respectively (Fig. 8b, c). Such electrodes have been utilized as self-powered sensors for real-time wave monitoring [67].

Yarn-like and fibrous structures possess stretchability, flexibility, and deformability when subjected to external forces. This unique property allows for optimal unidirectional material deformation, leading to high-performance output. For example, a coiled and twisted CNT yarn was utilized for wave energy harvesting by adjusting its spring index, which increased its deformation under external forces and led to reduced yarn stiffness (Fig. 8d). This enhancement provided an increase in the electrochemical available surface area, resulting in an improvement in output power. The CNT yarn with spring indexes of 0.29 and 0.79 showed an output power of 0.07 and 0.3 kW/kg, respectively, in 0.1 mol/L aqueous HCl (Fig. 8e, f) [69].

In addition, a buckled fiber made of folded multi-walled CNT (MWCNT) sheets exhibited an exceptionally compliant structure and low Young's modulus (2 MPa), which was 282 times lower compared to the previously reported coiled MWCNT yarn (Fig. 8g) [70]. The buckled fiber had microscale buckles formed by strain mismatch between the MWCNT sheet and the elastomeric fiber. As the pre-strain increased from 100% to 400%, the buckle size decreased from 38 to 16 μm, which resulted in a

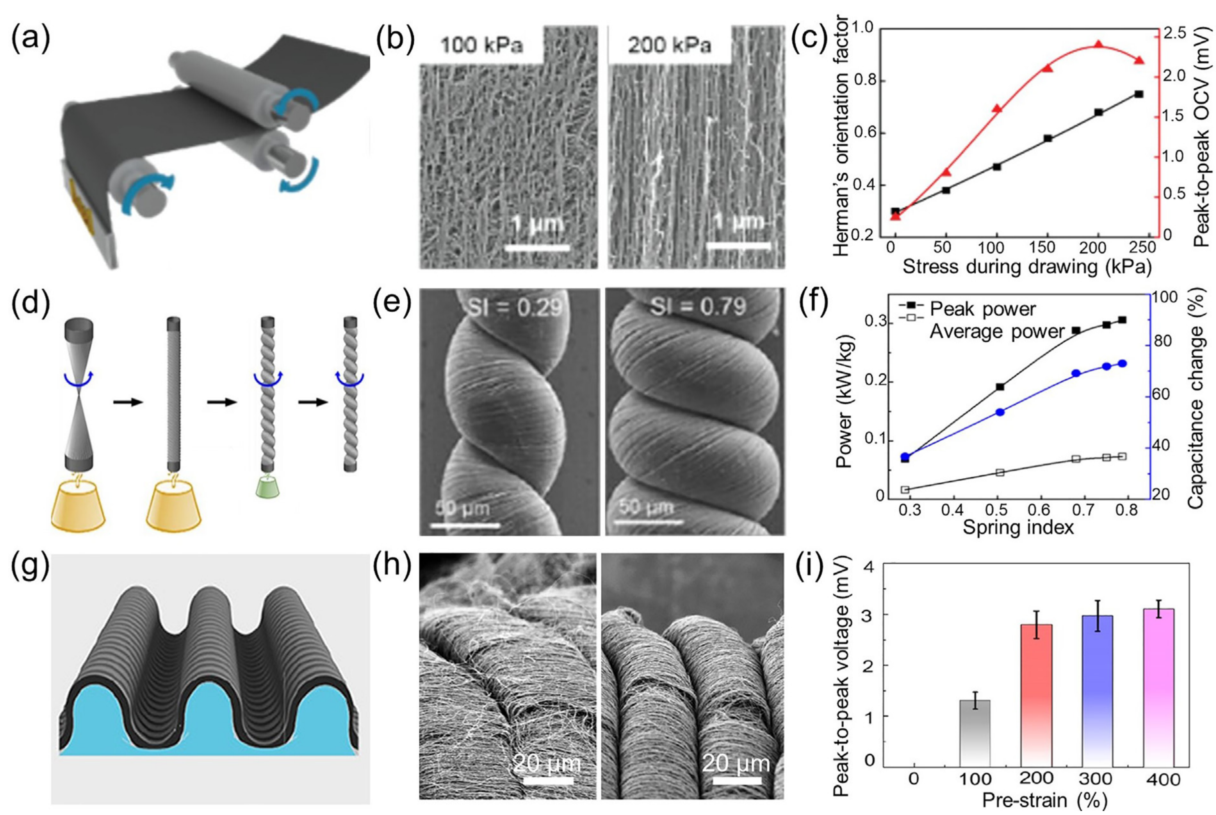


Fig. 8. (Color online) Structural modulation for the low-frequency performance improvement of electrochemical energy harvesters. (a) Schematic diagram of the fabrication of CNT sheet. (b) SEM images of CNT sheets prepared by different tensile stresses during draw (left, 100 kPa, right 200 kPa). (c) Peak-to-peak OCV of CNT sheets prepared by different tensile stresses during draw at 1 Hz. Reprinted with permission from Ref. [67], Copyright © 2020 Wiley. (d) Schematic diagram of the fabrication of CNT yarn. (e) SEM images of CNT yarns prepared by different load during coil. (f) Peak power of CNT yarns prepared by different load during coil at 1 Hz. Reprinted with permission from Ref. [69], Copyright © 2022 Wiley. (g) Schematic diagram of micro-buckle. (h) SEM image of CNT fibers with different pre-stretching conditions of 100% (left) and 300% (right). (i) Peak-to-peak voltage of CNT fibers with different pre-stretching conditions at 1 Hz. Reprinted with permission from Ref. [70], Copyright © 2022 American Chemical Society.

significant improvement in output voltage from 1.3 to 3.1 mV when the voltage was measured during the 1 Hz sinusoidal stretch to 100% strain in saline solution (Fig. 8h, i). This improvement in output performance was attributed to the increase/decrease in electrochemical available surface area caused by the folding and unfolding of microscale buckles during stretching/releasing cycles.

The yarn and fiber structure provide excellent dimensional matching for collecting mechanical energy in a single direction, but low-frequency mechanical energy often involves motion in multiple directions. Hence, a different approach is required. To address this issue, using a sponge structure is better because it has a three-dimensional (3D) network of pores and channels that can absorb mechanical energy from all directions. In addition, the sponge structure can adsorb more charge before and after applying force. For instance, a sponge-like MXene/rGO aerogel with multiple micro-mesoscopic channels and a large specific surface area showed a voltage output of several hundred millivolts and a high energy conversion efficiency of 43.2% at 0.2 Hz [71].

3.2.3. Structural modulation: piezoelectric energy harvesters

To improve the performance of piezoelectric energy harvesters at low frequencies, appropriate selection of the material is one of the key aspects [133–135]. PZT is often used because of its high-voltage coefficient and ability to be fabricated into thin films that are suitable for low frequency operation [32]. However, these films can be fragile. Instead, PZT nanofibers, made through electrospinning, possess high piezoelectric properties, flexibility, and strength [135]. Using these fibers to make piezoelectric cells can create energy harvesters that are flexible and efficient. For example, PZT nanofibers can be deposited onto platinum fine wire arrays on a silicon substrate with a PDMS protective layer (Fig. 9a, b). When a mechanical displacement is input, it could produce about 0.3 V of electricity (Fig. 9c) [136]. In addition, 2D layered materials with a non-centrosymmetric structure, such as MoS_2 and WSe_2, have drawn growing interest for applications in energy harvesting. Compared to conventional piezoelectric materials that retain their natural or pristine piezoelectricity, it is promising that the piezoelectric effect of 2D materials can be tailored through layer control or the design of artificial bilayer [133,134].

PVDF is a material commonly used in wearable piezoelectric energy harvesters, which can be fabricated into thin films, fibers, or yarns and formed into 2D or 3D shapes. For example, the direct-writing technique of near-field electrospinning was used to produce and place piezoelectric PVDF nanofibers on the working substrate (Fig. 9d, e). When repeatedly stretched and released, the fiber-based harvesters demonstrated output performances ranging from 5 to 30 mV and 0.5–3 nA. The energy conversion efficiencies of 45 harvesters were found to reach up to 21.8%, with an average of 12.5% (Fig. 9f). These values were significantly higher than those of typical harvesters made from experimental piezoelectric PVDF thin films (0.5%–4%) or commercial PVDF thin films (0.5%–2.6%). The improved effectiveness of the fiber-based harvesters can be attributed to the reduced number of defects during the near-field electrospinning process, which leads to a higher degree of crystallinity and chain orientation, resulting in a higher piezoelectric coefficient [34].

Furthermore, a 3D textile-based PVDF harvester was fabricated to harvest human motion energy (Fig. 9g). The 3D piezoelectric fabrics were produced using "3D spacer" technology, which consisted of high β-phase (~80%) piezoelectric PVDF monofilaments as spacer yarn interconnected between silver (Ag) coated polyamide multifilament yarn layers acting as the top and bottom electrodes (Fig. 9h). This device demonstrated a significantly higher

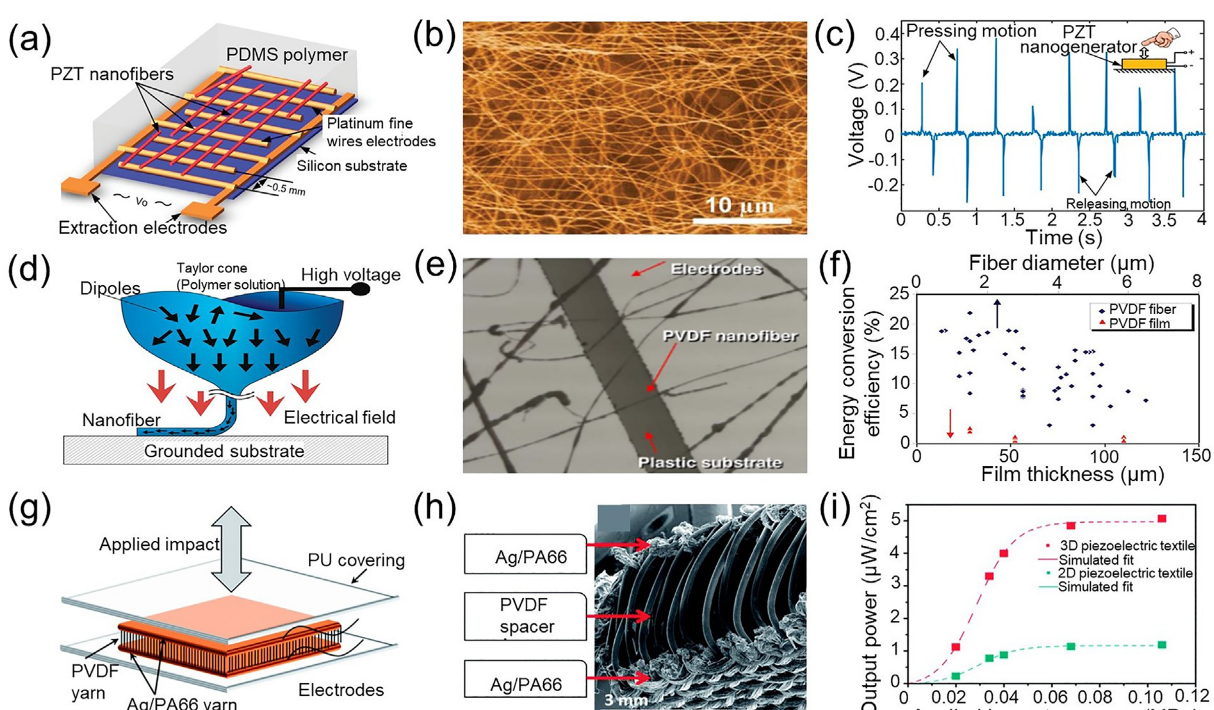


Fig. 9. (Color online) Structural modulation for the low-frequency performance improvement of piezoelectric energy harvesters. (a) Schematic diagram of PZT nanofiber harvester. (b) SEM image of PZT nanofiber mat across the interdigitated electrodes. (c) Output voltage of PZT nanofiber harvester when using a finger to apply load. Reprinted with permission from Ref. [136], Copyright © 2010 American Chemical Society. (d) The fabrication of PVDF fiber harvester. (e) Optical image of PVDF fibers deposited between two electrodes. (f) Energy conversion efficiency of PVDF fiber and PVDF film. Reprinted with permission from Ref. [34], Copyright © 2010 American Chemical Society. (g) Schematic diagram of the 3D fabric harvester. (h) Cross-sectional SEM image of the 3D fabric. (i) Output power of 2D and 3D fabrics. Reprinted with permission from Ref. [137], Copyright © 2014 The Royal Society of Chemistry.

output power under similar experimental conditions than the existing 2D woven piezoelectric structures (Fig. 9i) [137].

For dielectric elastomer energy harvesters, the structures of dielectric elastomer materials can be designed to be a 2D plate [95,138] or a 3D block [139]. The 2D plate is susceptible to large deformation under tension, which is suitable for harvesting low-frequency mechanical energy generated by wave motion [95]. The 3D block is prone to large deformation under compression, which is suitable for collecting low-frequency mechanical energy generated during walking and running [139].

3.3. Device design for the low-frequency performance improvement

Device designs refers to using different components (including the auxiliary components such as spring and packaging materials, etc.) or adjusting the parameters of each component (such as the number and length of windmill blades) to achieve optimal low-frequency output performance.

3.3.1. Device design: triboelectric energy harvesters

There are three strategies for improving the low-frequency performance of triboelectric energy harvesters from a device design perspective: (1) improving of the conversion of low-frequency input into high-frequency motion to increase output frequency, (2) enhancing the device response sensitivity to low-amplitude motion, and (3) maximizing space utilization by integrating multiple energy harvesting units. To effectively improve the low-frequency performance of the device, several approaches have been explored, such as assembling a spring inside the device [140,141], designing it as a rolling type [42,54,56,142], or designing it as a cantilever beam type [143–145].

A device with an integrated spring can store movement-induced energy, such as waves, and convert it into electricity. The spring can then convert low-frequency motion into high-frequency and long-period motion, making it easier to generate more electricity. For example, a harvester using a spring to temporarily store energy from friction showed that the addition of a spring increased the voltage by 22.8% and current by 29.6% produced by the device at a frequency of 1 Hz (Fig. 10a) [140]. Rolling-type harvesters can solve the low output problem of low-frequency motion by converting it into high-frequency motion using a rollable sphere inside an enclosed housing. The rolling motion of the sphere generates electrical energy through friction with the inner wall (Fig. 10b). Even after the mechanical trigger stops, the inertia of the ball allows it to continue rolling, enabling multiple cycles of energy conversion and improving efficiency. This design achieved a 95 V voltage and 1 μA current at 2.5 Hz [142]. A cantilever beam device was designed to improve low-frequency output performance in response to small vibrations, wind speeds, or waves. The device consists of a rectangular acrylic tube with two Al foils and a FEP film, with one side fixed and the other free. The periodic distance change between the Al foils and FEP film generates electrical energy, even at ultra-low wind speeds. The harvester achieved an output voltage of up to 100 V and a current of 1.6 μA [143].

In addition, multiple energy harvesting units integrated into a single device can improve space utilization and output performance per unit volume of the device. For example, a spherical whirling-folded harvester was designed with a 3D-printed substrate to harvest wave energy, which allowed for multiple energy harvesting units on each surface [150]. The flexible vortex structure responded easily to multiform wave excitation with an improved oscillation frequency, delivering a peak power of 6.5 mW at a wave frequency below 1.4 Hz and a wave height of 10 cm [150]. Similarly, a spring-assisted multilayer structure and a tower-like harvester with multiple units in one block were designed to improve output performance (Fig. 10c, d) [49,146]. The sawtooth multilayer structure and spring in the spherical triboelectric energy harvester enhanced output performance, while the rolling of PTFE balls in each cell of the tower-like harvester effectively converted mechanical wave energy into electrical energy [49]. For tower-like harvester, the integration of multiple units increased the power density of the harvester linearly from 1.03 to 10.6 W/m^3 at 2.4 Hz by increasing the units from 1 to 10 in one block [146].

3.3.2. Device design: electrochemical energy harvesters

To improve the low-frequency output of electrochemical energy harvesters, from a device design, the first aspect to considerate is the efficient absorption of mechanical energy in the corresponding low-frequency environment. Currently, there are three types of devices used for low-frequency mechanical energy harvesting: encapsulation-free [24,69,70], rigid encapsulation [67], and flexible encapsulation [66].

Encapsulation-free devices are preferred since they can directly collect energy from the environment, such as immersion in the oceans by using seawater as the electrolyte, and have superior output performance. Examples include an energy harvesting twistron yarn and a Pt mesh/CNT counter electrode that generated an average output power of 1.79 μW in seawater by harvesting the wave with the frequency ranged from 0.9 to 1.2 Hz [24]. Integrating multiple CNT yarn harvesters into a single device can also enhance output performance. For example, ten long twistrons were positioned parallel in the negative and positive compressibility directions of four wine-rack harvesters (Fig. 10e). When stretched at 35% and 1 Hz, each cell generated a peak OCV of 306 mV and a SCC of 1.97 mA. Connecting the cells in series and parallel increased the output OCV and SCC to 1.09 V and 7.31 mV, respectively [69]. In addition, in electrolyte-rich environments like human tissue fluids, encapsulation-free devices are preferred to minimize organ damage [70].

Rigidly packaged energy harvesters use a stiff material as an encapsulation or support material to capture mechanical energy in a specific direction. The rigid material protects the electrode material from external forces, making it suitable for various environments. For instance, a rigidly packaged self-powered sensor operated at a depth of 30 m in the marine environment, and the current output remained stable for 10,000 cycles at 1 Hz under 300 kPa [67].

In contrast, flexibly packaged harvesters with both deformable electrode and encapsulation materials can collect mechanical energy in multiple directions, making them ideal for wearable human motion energy harvesting. For example, a fibrous electrochemical energy harvester with CNT yarns as the working electrode and counter electrode was wrapped in parallel around a silicone rubber fiber. The encapsulation material was also silicone rubber, with a solid electrolyte gel containing 10 wt% polyvinyl alcohol and 0.1 mol/L HCl. This harvester exhibited good tensile properties, allowing 70% strain, and could be flexibly deformed in multiple directions. With impedance matching, it produced a maximum output power of 2.7 W/kg at a load resistance of 100 Ω at 1 Hz [66]. In summary, device design should be tailored to the specific application scenario in order to achieve optimal performance.

3.3.3. Device design: piezoelectric energy harvesters

To enhance the low-frequency performance of piezoelectric energy harvesters, a recommended approach is to improve frequency matching by either reducing the resonant frequency of the harvester [147,148,151,152] or transforming the low-frequency mechanical motion into high-frequency motion [153]. A widely adopted technique for achieving this is to design the har-

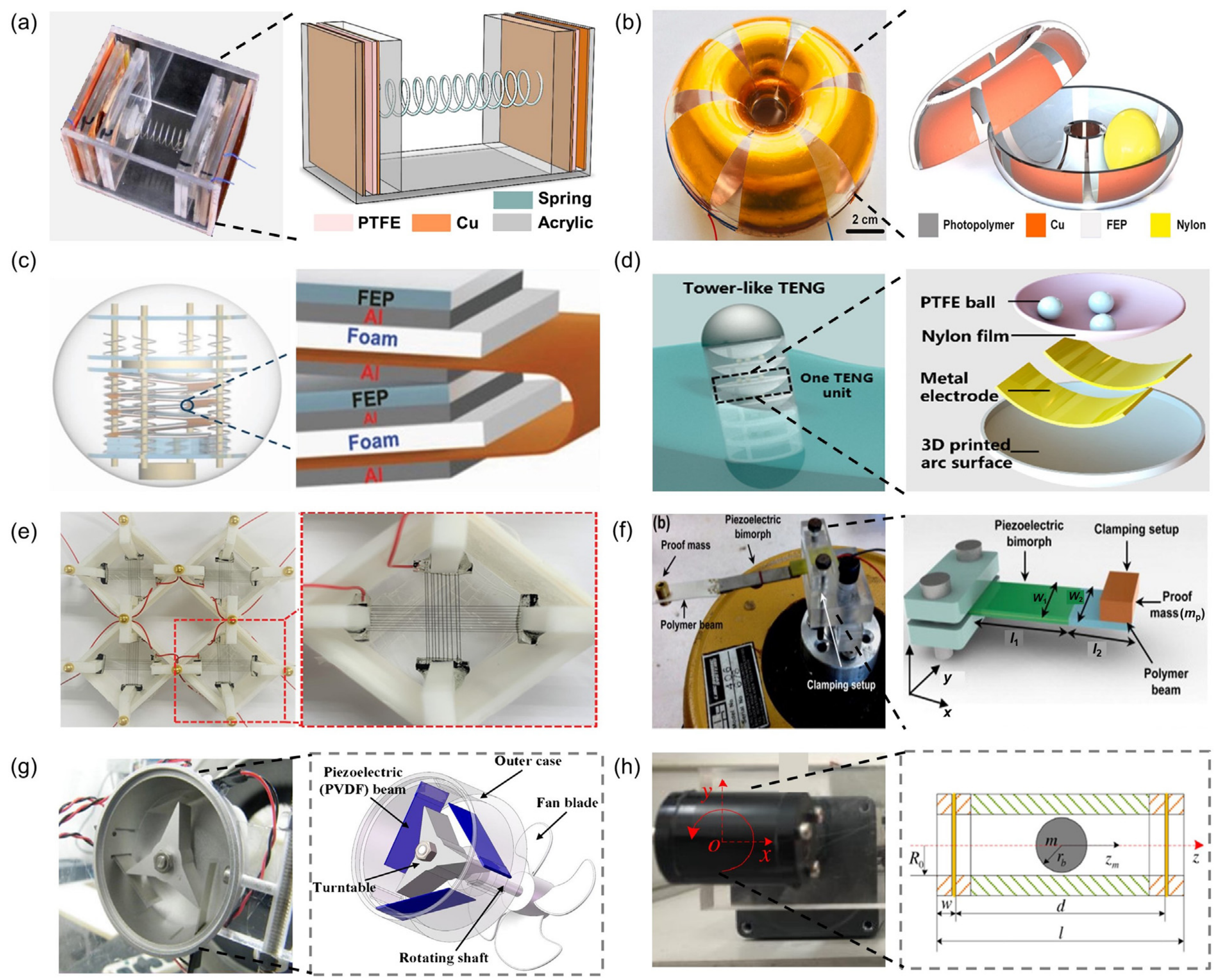


Fig. 10. (Color online) Device design of triboelectric, electrochemical, piezoelectric and dielectric elastomer energy harvesters. (a) Schematic diagram of a spring-assisted harvester. Reprinted with permission from Ref. [140], Copyright © 2016 Elsevier. (b) Schematic diagram of a rolling harvester. Reprinted with permission from Ref. [142], Copyright © 2019 Elsevier. (c) Schematic diagram of harvester with spring-assisted multilayered structure. Reprinted with permission from Ref. [49], Copyright © 2019 Wiley. (d) Schematic diagram of a tower-like harvester consisting of multiple units. Reprinted with permission from Ref. [146], Copyright © 2019 American Chemical Society. (e) Schematic diagram of wine-rack harvester. Reprinted with permission from Ref. [69], Copyright © 2022 Wiley. (f) Schematic diagram of composite cantilever. Reprinted with permission from Ref. [147], Copyright © 2013 Elsevier. (g) Schematic diagram of the rotational piezoelectric energy harvester. Reprinted with permission from Ref. [148], Copyright © 2017 Elsevier. (h) Schematic diagram of a vibration-impact structure. Reprinted with permission from Ref. [149], Copyright © 2020 Elsevier.

vester in the form of a cantilever beam structure, with a proof mass loaded at the free end of either a piezoelectric cantilever or diaphragm. However, despite this design, the high elastic modulus of the PZT and other piezoelectric materials often leads to the retention of a high resonant frequency.

This limitation can be overcome by employing a composite [147] or bending cantilever [151] design. For example, a composite cantilever was created by attaching a proof mass to the free end of a polymer cantilever connected in series with a piezoelectric bimorph (Fig. 10f) [147]. Incorporating the low-Young's-modulus polymer beam (0.5 GPa) resulted in a device with a lower resonant frequency than the piezoelectric bimorph alone (66 GPa). At a vibration acceleration of 0.1 g, the composite cantilever generated a maximum output power of 12.8 μW, significantly higher than the 4.1 μW generated by the piezoelectric bimorph alone. In a different example, an S-shaped piezoelectric PZT cantilever was fabricated with an S-shaped beam connected to a silicon proof mass to reduce the resonant frequency of the device [151]. Furthermore, a piezoelectric ocean-wave energy harvester consisting of a cantilever structure with a magnet and a rail with a metal ball was constructed, allowing for multi-directional vibration and energy harvesting [152]. When the harvester tilted from ocean waves, a metal ball rolled on a rail causing vibrations in the cantilever due to the attraction between the ball and the magnet. This allowed the harvester to harvest mechanical energy in both horizontal and vertical directions, unlike typical cantilevers which can only vibrate in one direction.

Using multiple cantilever beams can improve the output performance of piezoelectric energy harvesters. For example, a wind energy harvester with three PVDF cantilever beams, a fan blade, turntable, and rotating shaft generated a power of 2566.4 μW, significantly higher than 57.4 μW for the harvester with only one PVDF beam (Fig. 10g) [148]. Additionally, adding a spring can improve output performance by converting low-frequency mechanical action into high-frequency motion, such as in wind turbines where they convert rotational motion into linear vibration of two piezoelectricity-levers [153].

In addition, designing the device to be flexible is another approach to reduce its resonant frequency. A flexible design allows the device to deform easily under low-amplitude motion, making which it suitable for harvesting human motion energy [12,32]. For example, flexible self-powered sensors were developed by transferring a PZT sheet onto a flexible PET substrate to better capture the energy of human motion, which generated an OCV of 200 V and a SCC of 35 μA [32].

3.3.4. Device design: dielectric elastomer energy harvesters

From the perspective of device design, the strategy for improving the low-frequency performance of dielectric elastomer energy harvesters is to increase their capacitance change. Theoretically, the harvester exhibits the largest change in capacitance under equal biaxial deformation but implementing this deformation mode can be very complicated.

Most devices currently used for low-frequency scenarios, such as waves, wind, and the human body, employ uniaxial, pure shear, or circular inflatable deformation modes, which require further enhancement of their performance through device design [95,96,149]. For example, a rotating dielectric elastomer energy harvester was used to collect wind energy [149]. The device consisted of a small, two-bladed turbine designed to convert wind energy into rotational motion, which included a base, two blades, bearings, and a rotating shaft. At the end of the rotating shaft, a vibration-impact structure was symmetrically embedded (Fig. 10h). The vibration-impact structure consisted of a hollow cylinder, an internal rollable sphere, and a dielectric elastomer material at both ends of the cylinder. When the wind drove the blades to rotate, the ball impacted the dielectric elastomer material at both ends of the cylinder due to gravity and centrifugal force, thereby generating electrical energy. The output performance of this device depends on the impact of the ball onto the dielectric elastomer material. At a given wind speed, the distance, d, between the two dielectric elastomer materials can be adjusted to change the impact of the balls on the materials, thus optimizing the output performance of the device. When the wind speed is 1 m/s, the output power curve of the generating system can be divided into a two-sided impact region, a one-sided impact region, and a non-impact region as the value of d increases from 0.015 to 0.15 m. In the two-sided impact region, the output power remains relatively stable as d increases. This is because the energy per impact increases, despite the fact that the increase in d value leads to a smaller number of impacts. As d continues to increase, the ball impact decreases to one side or none at all, and the performance of the device decreases, or it fails to generate electrical energy. Therefore, the design of the separation d in this device plays a critical role in optimizing the generation of electrical energy.

4. Applications of low-frequency energy harvesting

The foregoing sections have examined the selection of materials, structural modulation, and device design with respect to the four energy harvesting mechanisms. The subsequent section endeavors to provide an extensive overview of the varied designs of energy harvesters in different application scenarios, specifically in relation to the low-frequency energy harvesting of wave energy, wind energy, and human motion energy, through exemplification.

4.1. Wave energy harvesters

Wave energy is the most abundant ocean energy, covering 94% of all ocean energy. The Earth's oceans make up 71% of the planet's surface, providing a large area for energy production. Wave power research is a priority for nations with significant oceanic resources such as the United Kingdom, where it is known as the "third energy source". Harnessing wave energy for electricity has the potential to advance marine industries, such as power supply, underwater robots, and radar equipment. However, harvesting wave energy presents challenges due to low frequency (below 2 Hz), small wave height, and low energy density, especially in land-based offshore environments.

4.1.1. Triboelectric wave energy harvesters

In addition to the customized electrode structure, effective device design plays a critical role in harnessing wave energy from the unpredictable and multi-directional ocean environment. A prime example of this is the use of triboelectric energy harvesters, which typically consist of two parts: an inner component and an outer casing. The outer casing shields the triboelectric material from environmental factors like humidity and is usually shaped as a sphere [39,42,49,51,54], ellipse [142], or cylinder [154,155] to capture energy from various directions. However, the design of the inner component is even more vital for achieving efficient energy conversion.

Common designs for the inner component include swing structures [154,155], rolling structures [42,54,142], and spring-assisted structures [39,49,51]. The swing structure prolongs the operational time of the device by continuing to generate electricity until the oscillation of the internal structure subsides, which amplifies the frequency and enhances the conversion efficiency. For example, a cylindrical triboelectric harvester with an internal swing structure generated a peak power of 4.56 mW at 1.62 Hz by swinging for 88 s and charged a capacitor of 220 μF under the wave triggering of 1.2 Hz and 10 cm (Fig. 11a) [154]. Rolled structures utilize a ball that rolls inside the device, rubbing against the material inside the device wall to generate electrical energy until it stops. This design also amplifies the output frequency and enhances performance. For instance, a spherical triboelectric harvester with a rolling soft liquid/silicon core was shown to power 26 green light emitting diodes (LEDs) with a 2 Hz input [54]. Spring-assisted structures store wave energy as potential energy in a spring and convert it into motion, thereby improving the output frequency [39,49,51]. A spherical triboelectric harvester with a spring-assisted multilayered structure generated a peak power of 6.79 mW at 1 Hz and powered dozens of LEDs through a four-harvester-array under wave motions. The multilayered structure also improved the space utilization of the device [39].

4.1.2. Electrochemical wave energy harvesters

Electrochemical energy harvesters can use electrodes designed as yarns [24,69], fibers [25], films [67], and sponges [71], as these structures can deform under low-frequency and low-amplitude wave motion, thereby changing the electrochemical available surface area and generating electrical energy. For instance, a yarn harvester made of a coiled MWCNT-yarn working electrode could convert mechanical energy through stretching and releasing by wave motion. An average output power of 1.79 μW was generated at frequencies ranging from 0.9 to 1.2 Hz, while a maximum peak power of 46.3 W/kg was obtained at 1 Hz to 30% strain [24].

Additionally, thin film and sponge electrodes are promising options for wave energy harvesting, as they can compress and release in response to wave heaving or lapping. For example, a harvester consisting of a MXene/rGO aerogel working electrode and a Pt mesh counter electrode was fabricated (Fig. 11b). The highly compressive ratio of up to 20% greatly promoted charge absorption, resulting in a peak power of 11.7 W/kg at 0.2 Hz in 0.5 mol/L NaCl with a high efficiency of 43.2%. The practical applicability of the harvester was demonstrated by successfully powering a red LED using a boost converter [71]. In another example, a CNT film was used as the working electrode of a self-powered sensor for wave monitoring, which achieved a peak power of 1.28 mW/m^2 at 0.02 Hz [67]. Notably, the compliance of a structure, as indicated by its low Young's modulus, is crucial in achieving high energy conversion efficiency.

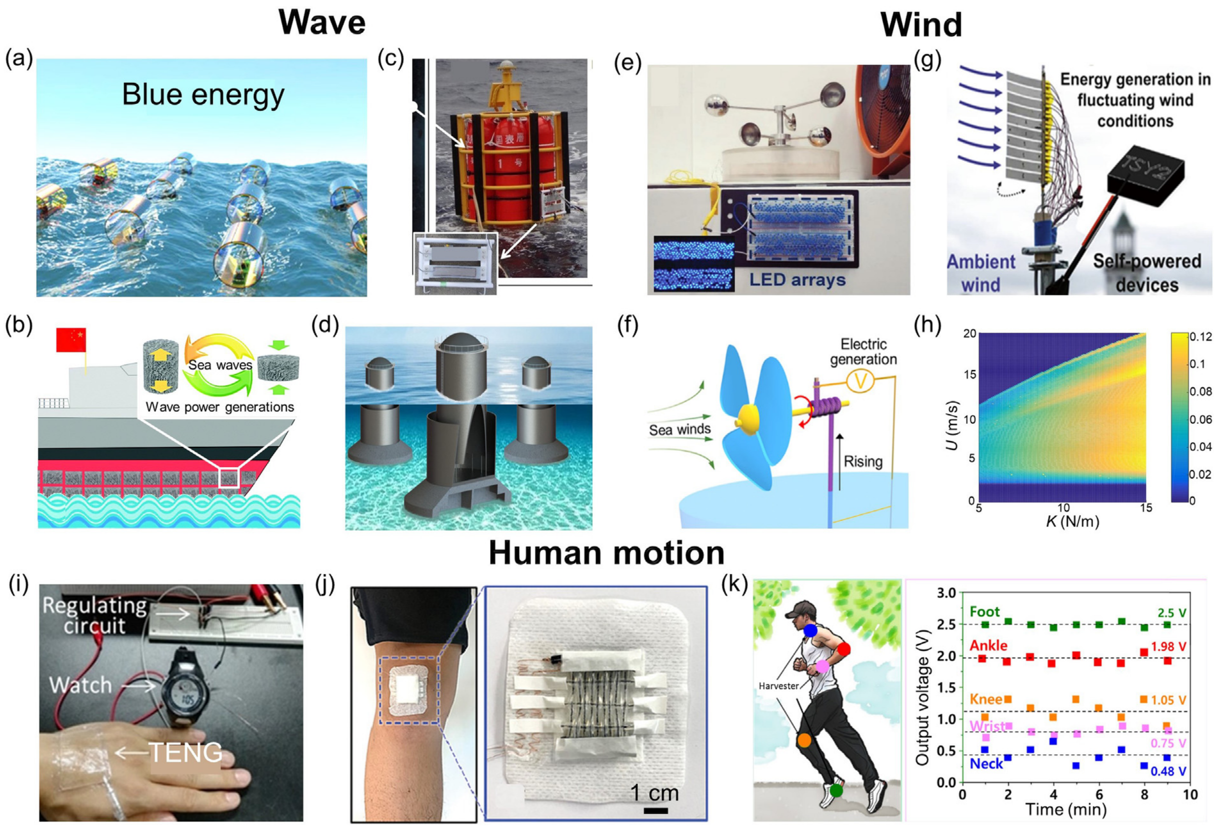


Fig. 11. (Color online) Applications of low-frequency energy harvesting. (a) Cylindrical triboelectric harvesters used for large-scale wave energy harvesting. Reprinted with permission from Ref. [154], Copyright © 2020 Wiley. (b) Schematic diagram of the MXene/rGO aerogel energy harvesters for application in ocean. Reprinted with permission from Ref. [71], Copyright © 2021 The Royal Society of Chemistry. (c) Photo of field test of a piezoelectric energy harvester. Reprinted with permission from Ref. [156], Copyright © 2017 Elsevier. (d) Schematic diagram of the detail structure of a dielectric elastomer energy harvester. Reprinted with permission from Ref. [95], Copyright © 2019 the Royal Society. (e) Photo of LEDs powered by triboelectric energy harvester. Reprinted with permission from Ref. [157], Copyright © 2021 Wiley. (f) Schematic diagram of CNT fiber harvester. Reprinted with permission from Ref. [25], Copyright © 2017 Wiley. (g) Photo of sensor powered by a piezoelectric energy harvester. Reprinted with permission from Ref. [158], Copyright © 2017 Elsevier. (h) Power of a vibro-impact harvester under different wind speeds. Reprinted with permission from Ref. [159], Copyright © 2019 Elsevier. (i) Photo of an electronic watch powered by a soft skin-like triboelectric energy harvester. Reprinted with permission from Ref. [10], Copyright © 2017 American Association for the Advancement of Science. (j) Photo of a real application of an energy harvester on human skin. Reprinted with permission from Ref. [66], Copyright © 2020 Wiley. (k) Voltage of the harvester under different locations on a human in the movement mode of running. Reprinted with permission from Ref. [12], Copyright © 2018 Elsevier.

4.1.3. Piezoelectric wave energy harvesters

Piezoelectric energy harvesters can be designed using laminated flexible structures [156] or swing structures [152]. One example of a laminated flexible piezoelectric energy harvester was developed to capture wave energy. This device is comprised of several layers, including a covered layer, upper electrode, piezoelectric paint, lower electrode, substrate layer, and elastic material. The laminated flexible harvester can oscillate easily due to the motion of ocean waves, while the covered layer and elastic material protect the harvester from wave impact damage. During a field test and near an oscillating wave propagator (mechanical toy fish), this harvester achieved a power of 175 μW/cm^3 at 2 Hz when the excitation amplitude was 30 mm (Fig. 11c) [156].

In another example, a piezoelectric swing structure energy harvester was fabricated, consisting of a cantilever, magnets attached to the free end of the cantilever, and a metal ball. The motion of the waves drives the harvester to sway, causing the cantilever to oscillate. Due to the rolling of the ball and the oscillation of the cantilever, this harvester could produce higher frequency motion to improve output performance, resulting in a maximum power of 68.9 μW at the excitation frequency of 0.5 Hz [152].

4.1.4. Dielectric elastomer wave energy harvesters

The circular inflatable mode is a widely used technique for harvesting wave energy using dielectric elastomer energy harvesters. This method involves utilizing the expansion and contraction of the dielectric elastomer material as the air pressure inside the chamber changes upon wave motions [95,96]. A system was developed to illustrate this method, comprising a U-shaped collector and a circular dielectric material harvester fixed on top of the air chamber (Fig. 11d). The collector used in this system has the water inlet section placed near the free surface, which provides the water column with large wave excitation forces. The harvester in this system generated a power output of more than 3 W at a frequency of 0.55 Hz, a wave height of 0.25 m, and a voltage of 9 kV [95].

To summarize, wave energy harvesting can employ electrode construction and device design to utilize four different mechanisms for energy harvesting. Among these mechanisms, electrochemical energy harvesters have garnered attention for their ability to harness energy directly from seawater using nanocarbon electrodes without the need for packaging. The low Young's modulus of their electrodes allows them to deform with low mechanical energy input. Particularly, the sponge structure stands out due to its porous channels, allowing for ion absorption and significant deformation from low-frequency waves. On the other hand, triboelectric energy harvesters offer various structural designs that can be applied to wave energy harvesting from different forms of motion. In addition, they have low material and manufacturing process costs, which is conducive to large-scale industrial production and practical application, thus making them a good candidate for wave energy harvesting.

4.2. Wind energy harvester

Wind power is a widely available mechanical energy source in nature with a global potential estimated to be 23 times greater than current electricity consumption. By 2030, wind power is projected to account for up to 6.5% of total electricity production. It can be especially useful in regions with scarce resources or challenging terrain. Offshore wind power generation is a critical sector for renewable energy development. The design of wind energy harvesting devices should indeed prioritize the efficient capture and conversion of low-speed wind energy.

4.2.1. Triboelectric wind energy harvesters

In the case of triboelectric energy harvesters, designs that incorporate rotational structures [157,160,161] and flow-induced vibration structures [143,145] are preferred for wind energy collection. Rotational structures are typically composed of a wind blade [161] or wind cup [157,160] connected to a rotating shaft that can transform wind energy into rotational energy. For instance, a dual-rotation shaft triboelectric energy harvester was created consisting of two sets of wind cups with varying arm lengths and a double-harvester module enclosed in a hermetic package. Wind cups with arm length, ranging from 12 to 20 cm and independent rotation shafts allowed for the efficient harvesting of wind speeds from 2.2 to 16 m/s, as demonstrated by powering LED arrays (Fig. 11e) [157].

In contrast, flow-induced vibration structures usually contain a cantilever beam that makes it feasible to achieve significant and high-frequency oscillations under low wind speed, thereby generating more electricity. For instance, a flow-induced vibration structure triboelectric energy harvester was fabricated, inside of which a CS mode cell consisting of nylon membrane, PET substrates, and Al electrodes was attached to a Y-shape cross-section galloping structure [145]. The galloping structure could vertically vibrate at low wind speeds, causing the materials to come into contact and generate electricity. The designed structure achieved an average power of 6 μW at a wind speed of 1.4 m/s, which could power several LEDs under both wind tunnel and open air-conditioner vent environments.

4.2.2. Electrochemical wind energy harvesters

Electrochemical wind energy harvesters operate by converting wind energy into rotational energy via a rotor. An illustration of this process is shown in Fig. 11f, where a CNT-fiber-electrode was attached to the axis of a fan to collect wind energy above the ocean [25]. Under natural wind conditions, this device could generate an output voltage of 60 mV. In addition, the electrolyte could be packaged within the device and linked to the windmill to capture wind energy. For example, a rGO@CNT/Pt twistron and electrolyte were sealed in a container and combined with a fan to form a wind energy harvester that could produce a peak power of approximately 150 W/kg [69].

4.2.3. Piezoelectric wind energy harvesters

To harvest wind energy, piezoelectric energy harvesters can be designed as flag [158] with a fixed edge and a free edge or rotational structures [148] with fan blades. The flag structure is capable of generating power over a wide range of wind speeds (3.5 to 9 m/s) without requiring optimal wind conditions. For instance, a piezoelectric flag was fabricated with a trailing edge fixed and a leading edge free to move, which successfully harvested ambient wind energy, achieving a power output of 5 mW/cm^3 at a wind speed of 9 m/s [158]. An outdoor setup of the piezoelectric flag was also demonstrated by harvesting energy from natural wind to power a temperature sensor (Fig. 11g).

In another example, a rotational harvester was designed with an external fan blade and three internal cantilevers, which generated a voltage of 160.2 V at a wind speed of 14 m/s [148]. Unlike rotational triboelectric energy harvesters, where the rotating shaft directly drives the friction or contact between two materials to generate electricity, the rotating shaft in the rotational piezoelectric energy harvesters drives the turntable or scotch yoke mechanism for motion. This provides an indirect route to induce vibration in the piezoelectric cantilever beam to generate electricity.

4.2.4. Dielectric elastomer wind energy harvesters

Dielectric elastomer energy harvesters commonly use the vibro-impact structure for wind energy harvesting [149,159]. This structure involves a rigid ball that impacts the dielectric elastic material, causing deformation and subsequent electrical energy generation. A harvester was constructed using such structure, and the cantilever beam and cuboid bluff body vibrated when wind passed through it, causing the ball to impact the dielectric elastomer materials at both ends of the cylinder. This harvester produced a power of 0.12 mW at a wind speed of 5 m/s (Fig. 11h) [159].

In another example, a rotational wind energy harvester was fabricated using a two-blade horizontal wind turbine and a vibro-impact structure consisting of a hollow cylinder and an inner ball embedded symmetrically at the end of the rotating shaft. As the wind drove the turbine to rotate, the inner ball moved between the two materials at both ends of the cylinder under the influence of gravity and centrifugal force. The rotation harvester produced an output power of 0.7125 mW at a wind speed of 3.99 m/s [149].

To summarize, all four types of energy harvesters aim to convert wind energy into electrical energy, typically in the form of rotational or vibrational energy. Windmills and cantilever beams are commonly utilized in these devices. When harvesting wind energy over land, electrochemical energy harvesters must consider electrolyte sealing. Additionally, dielectric elastomer energy harvesters require a high-voltage source, which may not be practical in remote areas. In contrast, triboelectric and piezoelectric energy harvesters do not require an electrolyte environment or high-voltage source, making them highly adaptable and flexible in design. Consequently, they can be integrated into various structures and offer promising potential for wind energy harvesting.

4.3. Human motion energy harvesters

Although not as prevalent as wave and wind energy harvesting, the development of human motion energy harvesting is a noteworthy area of study. It has the potential to power low-power electronics like smart watches, self-powered biomonitoring sensors, and smart shoes, which could replace conventional batteries. However, frequencies of human motion, such as those associated with running, walking, and swimming, are generally below 5 Hz and even lower (0.1 Hz) for some small movements within the body, such as stomach movements. Moreover, harvesting energy from human motion is made more complicated by the small displacements and multiple directions that characterize such motions. Despite these challenges, human motion energy harvesting remains an exciting field with tremendous potential for further research and development.

4.3.1. Triboelectric human-motion energy harvesters

To harness the kinetic energy produced by human motion, while ensuring that the energy harvesters are comfortable and versatile, researchers have developed human-motion triboelectric energy harvesters using elastomers and ionic hydrogels as the triboelectric layer and electrode, respectively [10,11]. For instance, a soft and skin-like triboelectric energy harvester was created using elastomers such as PDMS and an ionic hydrogel like polyacrylamide-LiCl hydrogel as the electrification layer and electrode, respectively [10]. This harvester generated a power density of 35 mW/m^2 at 1.5 Hz when a commercial Nylon film was used to create CS movement relative to the PDMS harvester. The harvester was placed on human skin and adjusted to capture frequencies ranging from 1 to 2 Hz, which effectively charged a capacitor and supplied power to an electronic watch (Fig. 11i).

In another example, researchers fabricated a flexible and stretchable triboelectric energy harvester by encapsulating MXene/polyvinyl alcohol hydrogel with silicone rubber. The MXene/polyvinyl alcohol hydrogel acted as the stretchable electrode and could be stretched up to 1800%, while the silicone rubber acted as the triboelectric layer and protected the hydrogel from water loss. When attached to the human elbow, this harvester was able to convert elbow movement into voltage signals, generating a voltage output of 80 V at a bending angle of 90° [11]. Most recently, the application of triboelectric energy harvesters has been extended to the biomedical field as implantable medical systems (pacemakers, neurological stimulators, etc.) which can be charged externally by vibrations, such as ultrasound [162–164].

4.3.2. Electrochemical human-motion energy harvesters

The applicability of electrochemical energy harvesters in human motion energy harvesting is due to the characteristics of nanocarbon-based electrodes. Nanocarbon-based electrodes, especially when fabricated in yarn [66,165] or fiber [70] form, exhibit excellent compliance, making them well-suited for use in human motion energy harvesting applications. This allows for easy integration into textiles and configuration in either series or parallel arrangements. Notably, twistron CNT yarn harvesters have been developed as wearable patches and attached to the human knee, yielding a peak power output of 2.7 W/kg at 1 Hz through impedance matching (Fig. 11j) [66]. Additionally, the inherent flexibility and softness of nanocarbon-based yarns or fibers minimizes tissue and organ damage when used inside the body. For instance, a CNT fiber with low Young's modulus (2 MPa) and high elasticity (up to 100%) was developed for soft organ motion tracking. This CNT fiber was able to operate successfully in a simulated stomach system, producing approximately 2 mV voltage when the stomach volume was charged through liquid injection or extraction [70].

4.3.3. Piezoelectric human-motion energy harvesters

As previously mentioned, traditional piezoelectric materials like $BaTiO_3$ and PZT are known for their stiffness and fragility. To overcome this challenge, researchers have developed nanocomposite-based flexible piezoelectric harvesters. For instance, one example of a flexible and durable piezoelectric nanocomposite is composed of $0.942(K_{0.480}Na_{0.535})NbO_3$-$0.058LiNbO_3$ particles and Cu nanorods embedded in PDMS. The piezoelectric nanocomposite is able to maintain its mechanical stability after 4000 cycles of displacement up to 5 mm of displacement, and can generate a power of 0.4 mW through hand slapping [166]. In another example, a harvester made with boron nitride nanosheet/PDMS composites as the active layer achieved a power density of 106 $\mu W/cm^3$ and generated a voltage of 1.98 V when attached to the human ankle (Fig. 11k) [12].

Although there have been relatively few reports on the development of dielectric elastomer energy harvesters, a commercial knee brace was developed to harvest human motion energy and could generate an average power of 3.13 μW during the walking motion [167]. Additionally, a stacked harvester was integrated into the heel to capture walking energy and generated a power of 1.8 mW when excited at 1.6 Hz [139]. Similarly, a flexible tube-structured harvester demonstrated deformation up to 100% and could be integrated into a knee brace to harvest 1.5 μJ of energy at 1 Hz under a poling voltage of 200 V [138].

To summarize, energy harvesters are designed to be stretchable and flexible so that they can deform naturally with human motion. Soft and skin-like triboelectric and piezoelectric materials have also been developed for human motion energy harvesting, but their performance needs further enhancement. Nanocarbon-based electrodes provide excellent flexibility, making electrochemical energy harvesters a suitable option for human motion. However, further advancements are required in packaging to ensure appropriate electrode deformation. On the other hand, dielectric elastomer energy harvesters, despite high applied voltage (several kilovolts) requirements and limited applications inside the human body, remain a viable option due to their elastic and lightweight properties.

5. Conclusion and perspective

5.1. Conclusion

This paper presents a comprehensive overview of the current state of research regarding triboelectric, electrochemical, piezoelectric, and dielectric elastomer energy harvesting for low-frequency mechanical energy. Based on the analysis, the following conclusions can be drawn.

(1) The energy harvesting techniques of triboelectric, electrochemical, piezoelectric, and dielectric elastomer harvesters exhibit significant potential for a wide range of applications in the field of marine industry, wearable electronics, and biomedicine. These methods have the capability to revolutionize energy generation, ease the burden on non-renewable forms of energy, and provide long-term benefit to the environment. For example, the continuous power supply is essential for the proper functioning of wearable devices, such as smartwatches and medical sensors. Traditional batteries are bulky and require frequent recharging. However, the four energy harvesting techniques mentioned above can utilize low-frequency mechanical energy generated by movements, such as arm movements and heartbeats, and transform it into electrical energy to power these wearable devices.

(2) The four types of energy harvesters have all demonstrated success in recovering low-frequency (≤5 Hz) mechanical energy, as depicted in Table 2. Currently, the lowest frequency at which mechanical energy can be retrieved is 0.02 Hz, and the energy harvesting efficiency ranges from 1.05% to 43.2%. Moreover, the voltage output can range from millivolts to several kilovolts.

(3) Recent research efforts in the field of energy harvesters have primarily focused on performance factors, such as output voltage, current, power, and energy conversion efficiency. Unfortunately, these studies have often overlooked a crucial factor known as the minimum excitation (Table 2). The minimum excitation refers to the minimum amount of energy input necessary to initiate and sustain the operation of energy harvesters. In applications involving low-frequency energy harvesting, the available input energy is typically extremely limited, such as vibrations from machinery or ambient environmental vibrations. Consequently, the ability of an energy harvester to function effectively with minimal energy input becomes vital for its practical implementation in low-frequency scenarios.

In essence, an energy harvester must possess the capability to detect and respond to even the slightest energy inputs in order to generate usable power. If an energy harvester necessitates a substantial amount of excitation to initiate its operation, it may prove impractical for deployment in situations where only a small

Table 2
Output performances of triboelectric, electrochemical, piezoelectric and dielectric elastomer energy harvesters at low frequency (≤5 Hz).

Type	Self-powered	Frequency (Hz)	Output performance				Minimum excitation (Pa)	Ref.
			Voltage (V)	Current (μA) #	Peak power (mW) #	Energy conversion efficiency (%)		
Triboelectric energy harvester	Yes	1	–	–	8.5	–	–	[50]
		1	–	–	7.96	–	–	[39]
		1	–	–	12.2	–	–	[49]
		1	419	56.7	–	–	–	[51]
		1.25	707	75.35	–	–	–	[52]
		1.43	–	1	10	–	–	[42]
		2.5	–	–	213.1 W/m^3	–	–	[56]
		0.017	500	–	–	1.05	–	[154]
		1.8	370	–	1.24	23.8	–	[168]
		2	350	5	–	–		[54]
		0.138	–	0.55	0.028	29.7	–	[106]
		1	–	–	0.090	–	–	[142]
		1.8	–	37.5	7.44	21.9	–	[9]
		1	–	–	0.33 W/m^2	–	–	[11]
		4	1300	–	7.4 W/m^2	–	–	[169]
		1.5	–	–	35 mW/m^2	–	1300	[10]
		1	41.9	56.7	4.1	–	–	[51]
		1	–	–	200 W/m^3	–	–	[170]
		2.5	–	–	40 W/m^3	–	–	[171]
		2	–	–	63.5 μW/ cm^2	–	–	[172]
Electrochemical energy harvester	Yes	1	–	–	46.3 W/kg	1.05	–	[24]
		1	0.38	–	460 W/kg	7.6	–	[69]
		1	0.105	–	181 W/kg	2.15	–	[72]
		0.2	0.25	–	11.7 W/kg	43.2	–	[71]
		4	–	–	5.3 W/kg	–	–	[66]
		1	0.55×10^{-3}	–	1.5 W/kg	–	–	[70]
		1	0.014	–	0.65 W/kg	–	–	[173]
		1	0.18	1.6 A/g	82 W/kg	–	–	[174]
		1	0.144	177.4 A/kg	41.9 W/kg	–	–	[175]
		0.02	2.2×10^{-3}	–	1.28 mW/m^2	–	10	[67]
Piezoelectric energy harvester	Yes	0.5	0.015	2×10^{-5}	0.001	5.08	–	[176]
		0.63	9.8	0.7	6.75×10^{-3}	–	–	[120]
		0.3	8.2	145	–	–	–	[33]
		2	–	–	175 μW/cm^3	–	–	[156]
		1.2	50	0.6 μA/ cm^2	–	23.18	–	[177]
		4	0.75	–	–	–	–	[178]
		0.6	200	35	–	–	–	[179]
		5	–	–	0.040	12.6	–	[12]
		0.27	12	1.2	–	–	–	[166]
		1	–	–	0.047	–	–	[180]
Dielectric elastomer energy harvester	No, need priming voltage (several kV)	0.55	–	–	3800	–	–	[95]
		0.15	–	–	–	9.5	–	[181]
		3	–	–	–	12	–	[182]
		1	200	–	0.033	–	–	[183]
		0.7	–	–	870	–	–	[96]

(1) The peak power values were obtained directly from the references or calculated from the presented data. When the power reported in the publications does not indicate whether it is a peak power or an average power, we assume that it is a peak power. (2) The values cannot be expressed in milliwatt (mW) and microampere (μA) due to the absence of information regarding the actual dimensions and mass of the samples as stated in the publications.

amount of ambient energy is available. Therefore, the concept of minimum excitation holds significant importance for low-frequency energy harvesters as it determines the level of ambient energy required to initiate and sustain their operation. Furthermore, it directly influences their viability in practical applications characterized by limited energy availability. By understanding and optimizing the minimum excitation requirements, researchers can enhance the performance and applicability of energy harvesters in various real-world scenarios.

(4) The current output power of the four types of energy harvesters is limited. Although it may suffice for some low-power applications, most applications require higher power. While electrochemical, triboelectric, and piezoelectric energy harvesters can operate as self-powered i.e., without the need for an external power source, dielectric elastomer energy harvesters require an additional applied voltage of several kilovolts to complete the working process (Table 2). Therefore, they are unsuitable for use in human body, marine, and similar environments.

5.2. Challenges

Although mechanical energy harvesters have shown promising performance for harvesting energy from low-frequency sources such as wave motion and human motion, significant challenges still remain in this area.

(1) One of the main challenges is the low amount of energy that can be harvested from low-frequency vibrations, which can limit the efficiency of energy conversion. However, researchers are making progress by developing novel materials and designs that can efficiently convert mechanical energy into electrical energy.

(2) Another challenge is related to the frequency, including the low input frequency of mechanical energy and the narrow frequency range of the energy harvesters. The low input frequency and amplitude of the mechanical energy add to the difficulty for energy harvesters to respond sensitively to the input, which reduces their energy conversion efficiency. In addition, current energy harvesters, such as piezoelectric energy harvesters, are

often designed to operate in a narrow frequency range, which can result in a mismatch between the frequency range in which they can operate and the frequency of the input mechanical action. This mismatch can lead to a loss of energy that cannot be recovered, further reducing the energy conversion efficiency.

(3) Mechanical losses present another challenge to energy harvesters. Components, such as springs, magnets, and frictional electric and piezoelectric materials can improve the low-frequency output performance of the device but also introduce mechanical losses, which can also reduce the energy conversion efficiency. The viscoelastic loss of materials in motion and the presence of frictional resistance between materials can further reduce the energy conversion efficiency.

(4) Electrical losses also affect the efficiency of energy conversion. The presence of resistance in other components in the circuit during conversion and storage can introduce electrical losses, reducing the energy conversion efficiency. Additionally, for energy harvesters that output a pulsed electrical signal, a rectifier diode is required, which has a threshold voltage (typically around 0.5 V). If the output voltage of the energy harvester is insufficient, the output becomes zero, which greatly reduces the overall energy conversion efficiency, particularly for devices with low output voltages, such as a single electrochemical energy harvester with an output voltage of up to a few hundred millivolts.

(5) Finally, the upper performance limit of the materials and the unstable performance also pose challenges to energy harvesters. The current upper performance limits of materials impose limitations on the potential of energy harvesters to fully replace batteries. For example, piezoelectric polymers with low inherent frequencies have small piezoelectric coefficients, which reduce the energy conversion efficiency of piezoelectric polymer-based devices. Although researchers have proposed methods to enhance the performance of energy harvesting output, such as introducing functional groups by surface functionalization to change the frictional electrical properties of the material, there are challenges in the practical application of these methods. For instance, the presence of unstable functional groups on the material surface can lead to unstable output performance, further reducing the energy conversion efficiency.

5.3. Perspective

In recent years, the development of low-frequency mechanical energy harvesters has emerged as a significant area of research and innovation. These devices possess the unique ability to effectively convert low-frequency mechanical vibrations into usable electrical energy, thereby enabling the powering of small electronic devices or charging batteries. To further advance this field, there are several key areas that warrant attention and exploration.

5.3.1. Development and design of new materials

Firstly, the development and design of new materials is crucial for advancing the upper performance limits of existing materials. This can be achieved through the development of green materials, functionalized materials, and composite materials that possess higher voltage coefficients, which can be evaluated through simulation technology.

One promising new material for low-frequency mechanical energy harvesting is a class of materials known as "relaxor" ferroelectrics. These materials have a unique crystal structure that allows them to efficiently convert mechanical energy into electrical energy. Research has shown that relaxor ferroelectrics can be used to develop energy harvesters that can generate significantly higher power outputs than traditional piezoelectric materials. Another promising material for low-frequency mechanical energy harvesting is a type of polymer known as electroactive polymers. Electroactive polymers are a class of materials that can deform in response to an electrical charge or generate an electrical charge in response to mechanical deformation. Researchers have shown that electroactive polymers can be used to develop highly efficient energy harvesters that can convert low-frequency mechanical vibrations into usable electrical energy.

5.3.2. Development of encapsulation technology

Encapsulation technology is an essential aspect of the development of low-frequency energy harvesters. It involves the development of materials and methods for encapsulating the devices, protecting them from the environment and ensuring their efficient and long-term operation.

In the case of wave energy harvesting, the harsh oceanic environment presents a significant challenge. The encapsulation materials must have good corrosion resistance and chemical stability to withstand the saltwater, humidity, and other harsh conditions. The materials must also be durable and long-lasting to ensure that the energy harvesters can continue to function effectively over an extended period.

For human motion energy harvesting, the encapsulation materials must be designed to ensure efficient harvesting of energy while maintaining comfort. This involves developing materials that are flexible, easily deformable, non-toxic, and biocompatible. Furthermore, these materials must be able to conform to the human body without causing restriction, while also ensuring that the energy harvesters remain securely in place.

5.3.3. Miniaturization and integration

Miniaturization and integration are important aspects of the development of low-frequency energy harvesters, especially for wearable devices. Wearable devices require energy harvesters to be lightweight, compact, and unobtrusive, and must be able to operate effectively within the confines of a small form factor. Micro/nanotechnology can be leveraged to achieve the necessary miniaturization of energy harvesters. This involves using micro and nanoscale manufacturing processes to create the electrode and packaging materials with high-precision control of their structure and performance. These processes can enable the creation of highly efficient energy harvesters that are small enough to be integrated into wearable devices and other systems.

In addition, the integration of energy harvesters into other devices and systems is an important direction for future development. This involves the incorporation of energy harvesters into existing products and systems to enable them to generate electricity from ambient energy sources. For example, energy harvesters could be integrated into smart home systems or Internet of Things devices to power them without the need for batteries or external power sources.

5.3.4. Development of highly sensitive energy harvesters

The development of highly sensitive energy harvesters is a crucial aspect of achieving maximum electrical power generation from ambient sources. To achieve this, the energy harvesting system must be designed to be highly sensitive to small inputs of energy. This can be accomplished through careful selection and coordination of transducers and other components.

Transducers are a key component of energy harvesters, as they convert mechanical energy into electrical energy. The careful selection of transducers can greatly impact the sensitivity of the system. For example, piezoelectric transducers have been widely used in energy harvesting systems due to their high conversion efficiency and sensitivity.

In addition to transducers, other components such as electrodes, packaging materials, and power management circuits can also impact the sensitivity of the system. The careful coordination of these components can ensure that the system is optimized for maximum sensitivity and efficiency.

Furthermore, the use of multiple transducers in parallel can be a promising approach to increasing system sensitivity. By using multiple transducers, the system can capture more mechanical energy from the environment, thereby increasing the overall efficiency and effectiveness of the system. This can be more effective than relying on a larger single transducer, which may be limited by its size and design.

Overall, the development of new materials and device architectures has been critical in advancing the field of low-frequency mechanical energy harvesting. These advancements have enabled researchers to develop highly efficient energy harvesters that are capable of generating significant amounts of electrical energy from a range of different sources. As new materials and device architectures continue to be developed, so does the potential/efficacy for the harvesting of low-frequency mechanical energy to expand their application to a wide range of fields.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Ming Xu conceived the idea and guided the review. Xingzi Xiahou conducted the literature search, manuscript writing and picture drawing. Sijia Wu conducted the literature search and picture drawing. Huajian Li assisted with the literature search and manuscript writing. Chen Chen assisted with the literature research and manuscript revision. Ming Xu and Xin Guo revised and edited the manuscript.

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