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Review

Flexible thermoelectric sensors for self-powered biosensing and environmental monitoring: From materials to integrated systems

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ABSTRACT

Based on the Seebeck effect, flexible thermoelectric technology can directly convert thermal energy into electrical energy by exploiting the small temperature gradient between the human body and the environment. Combining self-powered operation with highly sensitive thermal sensing, it can simultaneously meet the demands of energy supply and precise sensing, making it one of the key technologies driving the development of wearable smart devices. This review systematically and thoroughly examines the current research landscape of flexible thermoelectric sensors: it first establishes a theoretical framework for flexible thermoelectric energy conversion, elucidates the underlying working mechanisms, and addresses the structural design of flexible thermoelectric materials, evaluating their effects on thermoelectric performance, mechanical compliance, device integration, and application potential. It also discusses future trends and breakthrough directions. Drawing on cutting-edge data and representative case studies, it focuses on their integrated applications and practical performance in physiological signal and environmental monitoring. Finally, it summarizes the key technical challenges and identifies future directions such as material optimization, structural design, and intelligent integration, aiming to provide a reference for the development and practical deployment of flexible thermoelectric sensing technology.

1. Introduction

The rapid growth of the Internet of Things (IoT), wearable healthcare, and distributed environmental monitoring is driving sensor nodes toward continuous operation on the skin, in medical patches and implantable devices, and at remote environmental sites [1,2]. In these settings, conventional batteries impose charging or replacement requirements and can constrain device compliance, service life, and deployment at scale. Self-powered sensing therefore seeks to reduce dependence on external power by harvesting energy available in the operating environment [3,4]. Among available energy-harvesting approaches, thermoelectric (TE) conversion is particularly relevant when a usable temperature difference is present. Unlike triboelectric and piezoelectric harvesters, which typically depend on contact, motion, or deformation, and photovoltaic devices, which require illumination, a TE element converts a temperature gradient directly into a potential difference through the Seebeck effect. While other self-powered routes, such as supercapacitor-integrated sensors, have also been explored [5], they primarily rely on stored energy rather than direct thermoelectric conversion. Such energy-storage units may complement thermoelectric sensing, but their integration into unified thermoelectric sensing platforms remains an open direction. Body heat and thermal gradients at industrial or environmental interfaces can thus provide inputs without requiring continuous mechanical actuation or illumination; in practice, output remains governed by the available temperature difference and the thermal pathway [6].

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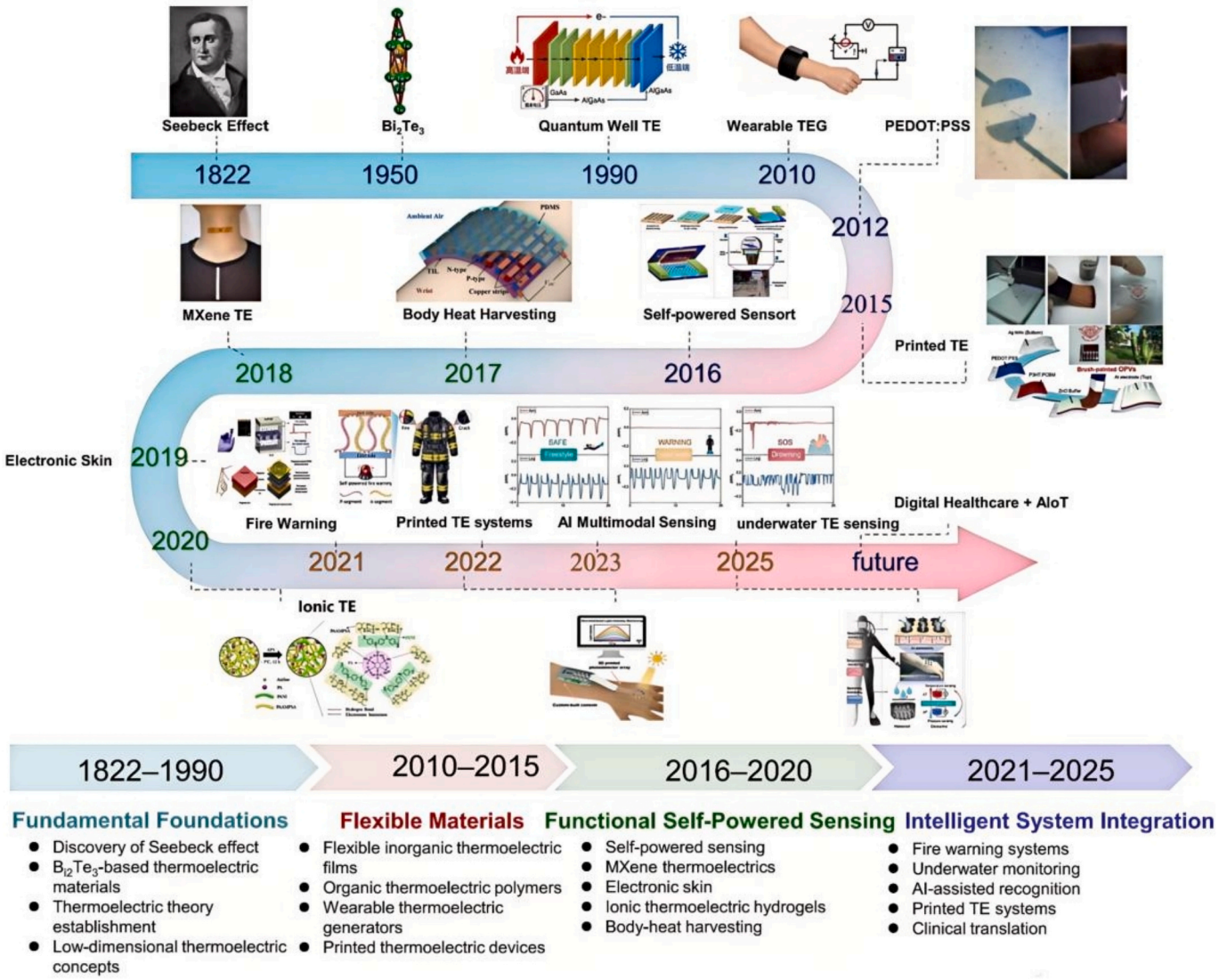


Fig. 1. Technological Development Roadmap of Flexible Thermoelectric Sensors [9–19]. Reproduced with permission from Ref. [9]. Copyright 2023 Wiley. Reproduced with permission from Ref. [10]. Copyright 2012, Springer-VBH. Reproduced with permission from Ref. [11]. Copyright 2015,WILEY-VCH. Reproduced with permission from Ref. [12]. Copyright 2022, Wiley-VCH GmbH. Reproduced with permission from Ref. [13]. Copyright 2019 Elsevier. Reproduced with permission from Ref. [14]. Copyright 2016 Elsevier B·V. Reproduced with permission from Ref. [15] Copyright 2019 Elsevier. Reproduced with permission from Ref. [16]. Copyright 2017 Elsevier. Reproduced with permission from Ref. [17]. Copyright 2024, Donghua University, Shanghai, China. Reproduced with permission from Ref. [18]. Copyright 2025 Wiley-VCH GmbH. Reproduced with permission from Ref. [19]. Copyright 2026 Springer Nature.

This dual role of temperature is particularly relevant to biosensing and environmental monitoring because temperature can serve both as an energy source and as the measurand. On-body devices may harness body–ambient heat flow while tracking local temperature or heat-flow changes; in environmental settings, thermal events such as fire-related heating or spatial temperature variations can produce interpretable thermovoltage signals. These functions should not be conflated: when the target is biochemical, such as a sweat analyte, thermoelectric transduction generally needs to be coupled to a recognition or auxiliary sensing element, whereas direct thermoelectric sensing reads a thermal gradient. This distinction helps explain why flexible TE platforms are relevant to thermal monitoring and can also serve as power units within broader sensing systems [7,8].

Despite this promise, practical performance cannot be inferred from the conversion mechanism alone. Small body–ambient temperature differences, thermal contact resistance, parasitic heat flow, mechanical deformation, and ambient fluctuations can alter output and long-term reproducibility. Moreover, electronic and ionic TE devices generate thermovoltage through different carrier-transport processes; their contributions should therefore be interpreted in relation to the sensing task and device configuration, rather than treated as interchangeable materials or ranked by a single metric. Recent reviews have surveyed wearable thermoelectric materials and devices, as well as thermoelectric biosensing [6]. Building on these foundations, the present review emphasizes the links among charge-carrier mechanisms, flexibility-engineering strategies, device architectures, and the distinct roles these systems can play in self-powered biosensing and environmental monitoring. In this context, Fig. 1 summarizes representative milestones in flexible thermoelectric sensing, from advances in material systems toward conformable device structures and application-oriented integration.

Over the past decade, research on flexible thermoelectric (TE) sensing has broadened in both material composition and device architecture. Investigations have encompassed thin-film inorganic TE materials such as Bi_2Te_3, solution-processable conducting polymers such as PEDOT:PSS, carbon-based nanomaterials, elastomer composites, fiber/

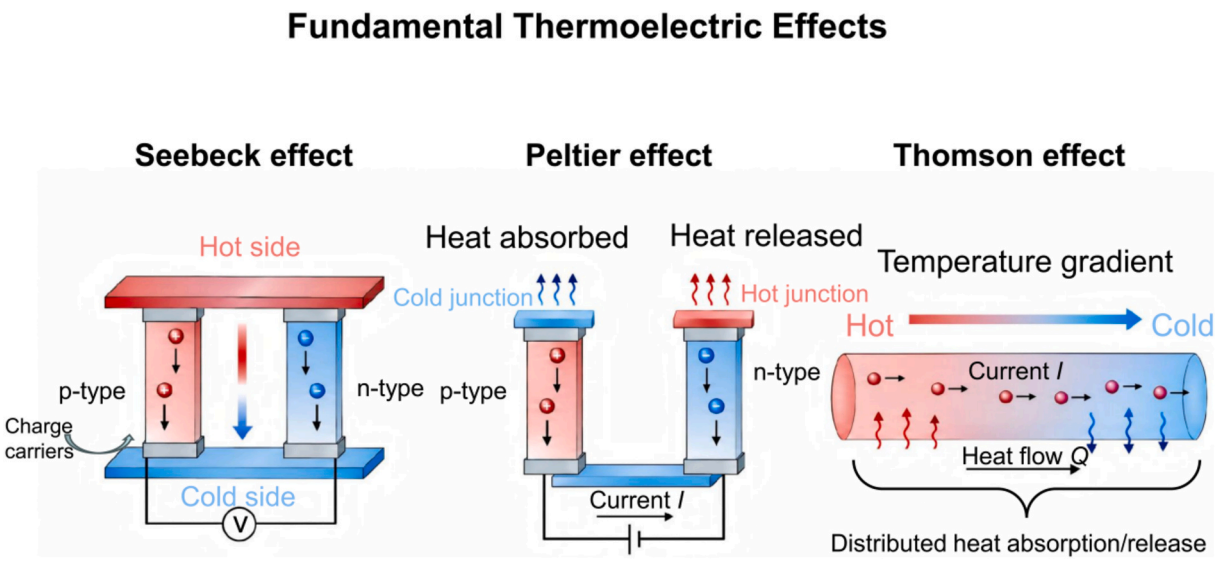


Fig. 2. Schematic illustration of the three fundamental electronic thermoelectric effects.

textile architectures, and ionic TE systems. Reported applications have likewise expanded beyond temperature sensing to include wearable health monitoring, electronic skin, fire detection and early warning, underwater sensing, sweat-based biochemical analysis, and biomimetic temperature and thermal nociception in robotic systems. Collectively, these studies form a substantial and continuing body of literature. Many existing reviews organize the field primarily by material composition or application area, while introducing working mechanisms as background at the beginning of the review. Although these approaches provide broad coverage, the relationships among material characteristics, device design, and application performance may remain distributed across separate sections. This is particularly relevant to electronic and ionic TE systems, which differ in their signal-generation mechanisms and operational roles.

Compared with existing reviews, this review aims to make three main contributions. First, it provides an integrated mechanistic framework that distinguishes electronic and ionic TE sensing. Second, it reorganizes flexible TE materials by flexibility-enabling strategies rather than by composition alone. Third, it systematically relates material and device characteristics to application-specific requirements while separating TE transduction from auxiliary functions. These contributions are implemented through four organizational principles. First of all, electronic and ionic TE sensing mechanisms are discussed in a dedicated section, establishing the basis for understanding their signal generation before the materials discussion. Second, materials are organized according to how flexibility is achieved, rather than solely by chemical composition, and are discussed through five representative strategies: thin-film processing and nanoengineering, island–bridge architectures, integration with elastic substrates and gel matrices, intrinsically stretchable designs, and fiber/textile or three-dimensional porous architectures. Third, the application sections relate material and device characteristics to task-specific requirements. The roles of electronic and ionic TE materials are identified separately according to the reported device configurations and operating conditions; complementary functions are described where a study demonstrates their integration, rather than being assumed across all applications. Fourth, the outlook organizes future development across three interconnected levels-materials, devices, and systems.

2. Sensing mechanisms of flexible thermoelectric sensors

Thermoelectric effects, which convert temperature differences into electrical signals, provide the fundamental basis for subsequent material selection and device design [20–22]. Here, we discusses two distinct operating mechanisms. The first is the classical thermoelectric effect based on electron or hole transport, including the Seebeck effect, Peltier effect, and Thomson effect. The second is the ionic thermoelectric effect, which has attracted increasing attention in recent years and is primarily governed by ion migration or interfacial electrochemical reactions [23,24]. Because the transport mechanisms of these two categories differ fundamentally, they are discussed separately below.

2.1. Fundamental mechanisms of electronic thermoelectric effects

Thermoelectric phenomena are generally described by three fundamental effects, such as the Seebeck, Peltier, and Thomson effects. The fundamental mechanism of electronic thermoelectric effects is summarized in Fig. 2. Among them, the Seebeck effect is the most widely exploited in sensing and energy-harvesting applications. When a temperature gradient exists within a conductive material, differential migration of charge carriers occurs, resulting in the generation of an electrical signal [7,20–22]. A temperature gradient induces carrier diffusion from the hot region to the cold region because of the difference in carrier energy distribution. This directional movement of charge carriers leads to charge accumulation at opposite ends of the material, generating a potential difference that, when measured, is referred to as the Seebeck voltage [6]. Consequently, a temperature gradient can be directly converted into an electrical signal. The thermoelectric figure of merit (ZT) is widely used to evaluate thermoelectric performance. ZT serves as an important indicator of the potential efficiency of thermoelectric materials. The expression for ZT is given by:

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

where S, σ, and κ denote the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively [25–27]. The higher the ZT value, the better the thermoelectric performance of the material and the greater its contribution to improving energy conversion efficiency (η). Therefore, an ideal thermoelectric material should possess a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity [27]. These three physical parameters(s , σ , and k) are strongly coupled to one another, making the optimization of thermoelectric performance extremely challenging. For metallic systems, the Wiedemann–Franz law relates electrical conductivity to electronic thermal conductivity. This implies that increasing the electrical conductivity is often accompanied by an increase in electronic thermal conductivity,

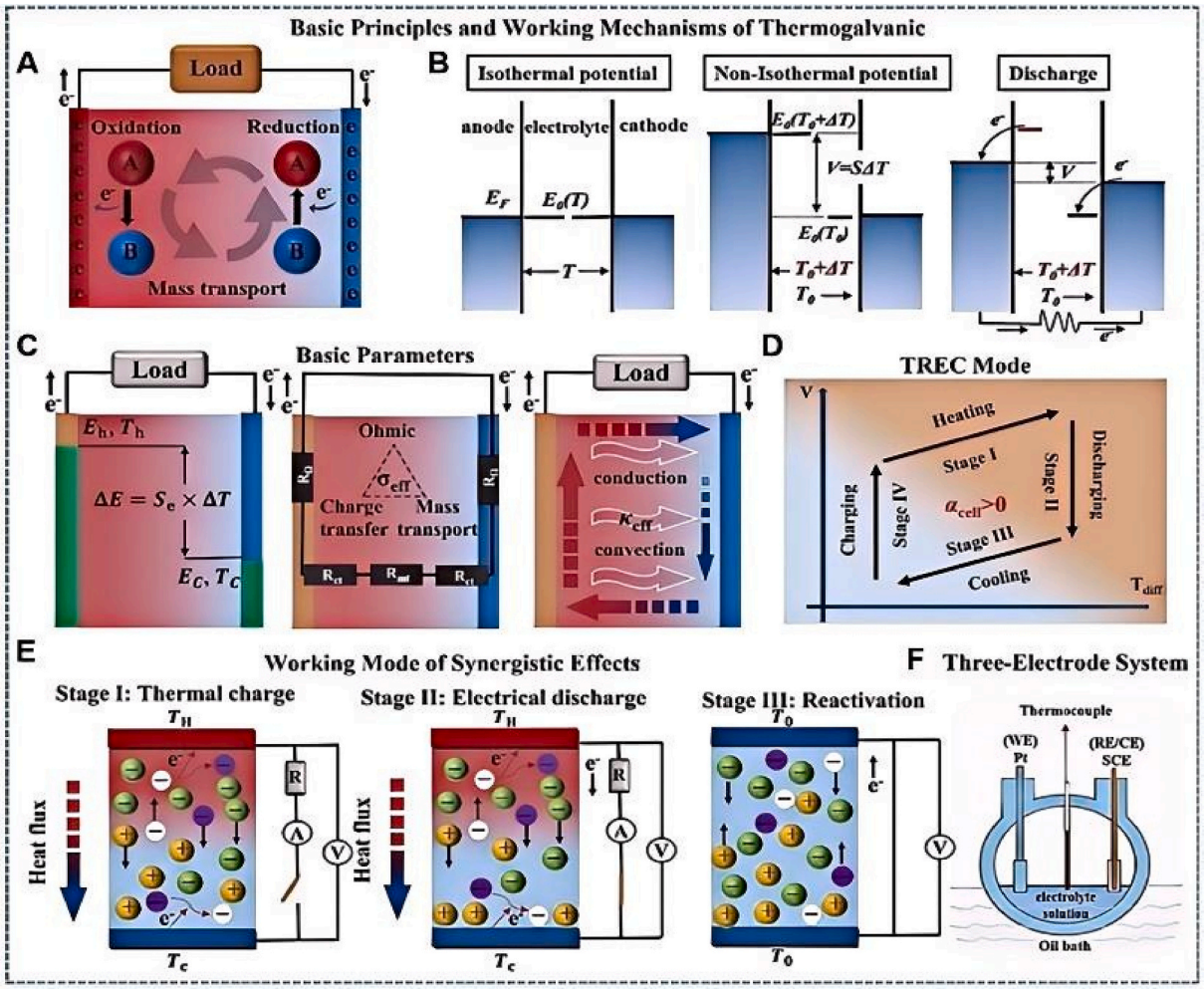


Fig. 3. Fundamental Working Principles and Synergistic Mechanisms of Ionic Thermoelectric Thermogalvanic Systems. (A) Schematic illustration of the redox reactions and ion transport in a thermogalvanic cell. (B) Evolution of electrode potential under isothermal, non-isothermal, and discharge conditions. (C) Key factors governing the output performance of thermogalvanic devices, including thermoelectric potential, charge transport, and heat transport. (D) Operating principle of the Thermal Regenerative Electrochemical Cycle (TREC). (E) Thermodiffusion-thermogalvanic synergistic mechanism. (F) Schematic illustration of the three-electrode measurement system. (A-F) Reproduced with permission from Ref. [46]. Copyright 2020 American Chemical Society.

which limits further improvements in *ZT* [28]. This relationship can be described by the following equation:

$$Ke\rho = LeT$$

where *Le* is the electronic Lorenz number [29]. In semiconductor materials, *K* consists of two contributions, one of which is the electronic thermal conductivity (k_e) and the other is the lattice thermal conductivity (k_l). Therefore, the use of thermoelectric semiconductor materials provides a conventional approach to overcoming this limitation, thereby significantly enhancing the conversion efficiency of the thermoelectric effect and enabling its practical applications. Furthermore, an increase in charge-carrier concentration generally enhances electrical conductivity but tends to reduce the Seebeck coefficient. Therefore, semiconductor thermoelectrics offer additional degrees of freedom for decoupling electrical and thermal transport. The Peltier effect and the Thomson effect, as important components of the thermoelectric effect, correspond respectively to the reverse conversion between electrical energy and thermal energy and to the absorption or release of heat when an electric current passes through a conductor. Although less frequently employed in thermoelectric sensing, these effects play important roles in thermal management and cooling technologies. Together with the Seebeck effect, they form the complete theoretical framework of thermoelectric phenomena.

2.2. Ionic thermoelectric sensing mechanisms

Electronic thermoelectric effects provide a well-established theoretical framework for understanding the conversion between temperature differences and electrical signals. Sensing technologies based on this mechanism have demonstrated excellent performance under stable temperature gradient conditions. However, when these materials are extended toward flexible and wearable applications, they face certain limitations in mechanical compliance, and their output voltage under small temperature differences is often relatively low. Under such circumstances, ionic thermoelectric systems have attracted increasing attention from researchers due to their distinct energy conversion mechanisms [23]. Unlike electronic thermoelectric systems, ionic thermoelectric materials utilize temperature gradients to drive the directional migration of ions or induce temperature-dependent redox reactions at electrode/electrolyte interfaces, thereby converting thermal energy into electrical energy. Since the entropy change associated with ion migration is significantly greater than that involved in electronic transport, these materials typically generate thermovoltages that are one to two orders of magnitude higher than those of electronic thermoelectric systems [24].

Beyond thermoelectric conversion, triboelectric nanogenerators integrated with flexible supercapacitors have also been developed as self-

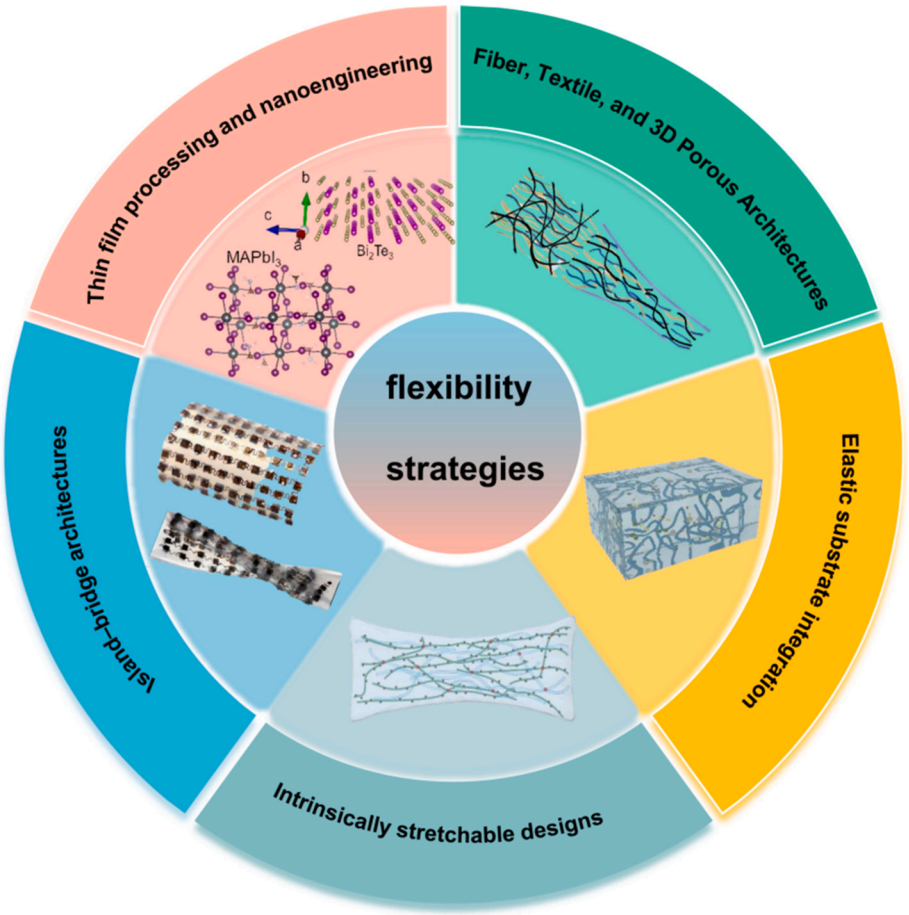


Fig. 4. Five engineering strategies for realizing flexibility in thermoelectric materials and devices. Reproduced with permission from Ref. [47]. Copyright 2025 Elsevier. Reproduced with permission from Ref. [48]. Copyright 2020 American Chemical Society. Reproduced with permission from Ref. [49]. Copyright 2024 Wiley - VCH GmbH. Reproduced with permission from Ref. [50]. Copyright 2025 Springer Nature. Reproduced with permission from Ref. [51]. Copyright 2025 Wiley -VCH GmbH.

charging power systems for wearable electronics [30]. However, these approaches rely on mechanical motion or contact, whereas thermoelectric conversion is uniquely suited to static temperature gradients and can simultaneously serve as a sensing mechanism. This characteristic enables ionic thermoelectric materials to exhibit unique potential for harvesting the weak temperature gradients available on the human body surface and developing highly sensitive self-powered sensors [4,31]. Depending on the energy conversion mechanisms, ionic thermoelectric systems can be classified into several categories, including thermodiffusive, thermogalvanic, and hybrid systems that combine both mechanisms. Among them, thermogalvanic systems have attracted extensive attention due to their reversible redox reactions. In these systems, redox couples dissolved in the electrolyte undergo temperature-dependent electrochemical reactions driven by a temperature gradient. Oxidation occurs at the hot end, while reduction occurs at the cold end, enabling continuous current output through an external circuit [8,32,33]. Fig. 3 illustrates the fundamental working principle of thermogalvanic systems together with their synergistic energy-conversion mechanism.

As schematically illustrated in Fig. 3A,B, a thermogalvanic device typically comprises two electrodes separated by an electrolyte containing a reversible redox couple. Under isothermal conditions, identical electrochemical potentials are established at both electrodes, resulting in thermodynamic equilibrium and zero output voltage. When a temperature gradient is applied, this equilibrium is broken, causing oxidation to proceed preferentially at the hot electrode while the complementary reduction reaction occurs at the cold electrode. Because the reaction entropy of the reversible redox couple varies with temperature, a temperature-dependent electrode potential is established between the two electrodes. Upon connection of an external circuit, electrons flow from the hot electrode to the cold electrode through the external load, while the redox species continuously undergo electrochemical cycling within the electrolyte to maintain charge neutrality. This coupled electron–ion transport enables sustained electrical output under a stable temperature gradient, thereby achieving continuous conversion of thermal energy into electrical energy [34,35].

Compared with conventional electronic thermoelectric devices, in which thermoelectric voltages originate from carrier diffusion, thermogalvanic systems exploit reversible electrochemical reactions to achieve sustained electrical output under a persistent temperature gradient. This unique operating mechanism makes them particularly well suited for harvesting low-grade thermal energy and powering next-generation flexible self-powered sensors [36,37]. Fig. 3C further illustrates the key factors governing the output performance of thermogalvanic devices. In addition to the thermoelectric potential, device performance is jointly determined by charge transport and heat transport processes [38]. Specifically, the ohmic resistance governs the electrical conduction of electrons and ions, the charge-transfer resistance reflects the reaction kinetics at the electrode/electrolyte interface, and the mass-transfer resistance is closely associated with ion diffusion and the establishment of concentration gradients [39]. Meanwhile, the effective thermal conductivity determines the ability of the device to maintain the temperature difference between the hot and cold electrodes, whereas thermal convection weakens the temperature gradient

and consequently reduces the practical output performance. Therefore, enhancing ion-transport efficiency, optimizing the electrochemical reactions at the electrode/electrolyte interface, and minimizing thermal losses are key strategies for improving the output performance of thermogalvanic devices.

To further improve the utilization efficiency of low-grade thermal energy, researchers have recently proposed a Thermal Regenerative Electrochemical Cycle (TREC) operating mode, as illustrated in Fig. 3D. This operating mode exploits the temperature-dependent variation in the electrode potentials of reversible redox couples to achieve cyclic conversion between thermal and electrical energy through successive heating, discharging, cooling, and charging processes. As a result, it enhances the utilization efficiency of low-grade thermal energy and provides a promising strategy for the continuous power supply of flexible thermoelectric devices [40,41]. Meanwhile, to simultaneously achieve a high thermoelectric potential and sustained electrical output, researchers have further developed a thermodiffusion–thermogalvanic synergistic mechanism, as illustrated in Fig. 3E. In this system, thermal charging is first induced by a temperature gradient, after which the stored electrical energy is released through an external load. Upon restoration of the initial temperature, the ion distribution is re-established, enabling three consecutive processes-thermal charging, discharging, and reactivation. This synergistic operating mode significantly enhances both the output stability and the cycling performance of the system [42,43].

In addition, to accurately evaluate the intrinsic thermoelectric performance of thermogalvanic systems, a three-electrode measurement configuration, as illustrated in Fig. 3F, is commonly employed. By independently monitoring the temperature-dependent electrode potential of the working electrode with respect to the reference electrode, while using a counter electrode to complete the electrochemical circuit, this method effectively eliminates parasitic thermodiffusion-induced potentials and enables a more accurate determination of the intrinsic thermogalvanic Seebeck coefficient. Consequently, it provides a standardized approach for evaluating and comparing the thermoelectric performance of different ionic thermoelectric materials and devices [44,45].

Overall, electronic and ionic thermoelectric effects correspond to different application scenarios. Electronic thermoelectric systems possess advantages in conventional thermoelectric power generation and rapid temperature response due to their mature material foundations and stable carrier transport characteristics. In contrast, ionic thermoelectric systems exhibit unique value in weak temperature gradient harvesting and bio related sensing owing to their high thermoelectric potentials and excellent interfacial compatibility. The differences in their transport mechanisms, with the former relying on the migration of electrons or holes and the latter depending on ion diffusion or interfacial reactions, not only determine the aforementioned performance characteristics but also give rise to distinct strategies for achieving flexibility.

3. Materials and flexibility strategies

The differences in the transport mechanisms of electronic and ionic thermoelectric effects give rise to distinct challenges in flexible design. Electronic materials rely on charge-carrier transport, and bending may disrupt the continuity of conductive pathways. Ionic materials rely on ion migration and interfacial reactions, so deformation more directly affects the structural integrity of gel networks and their ability to retain solvents. To address these challenges, researchers have developed five routes to flexibility, as illustrated Fig. 4: thin film processing and nanoengineering, island–bridge architectures, integration with elastic substrates, intrinsically stretchable designs, and one dimensional fibers and textiles combined with three dimensional porous structures. Representative studies of electronic and ionic systems along these routes are presented separately, and their performance metrics are not ranked across different mechanisms.

3.1. Thin film processing and nanoengineering for flexibility

Thin-film processing and nanoengineering provide a direct route to introducing flexibility into high-performance thermoelectric materials. The central strategy is to reduce bending stiffness by decreasing the thickness of the thermoelectric layer, tuning the material composition, introducing defects, and engineering interfaces. This approach is particularly suitable for inorganic semiconductors, which exhibit excellent charge-carrier transport in bulk form but are intrinsically rigid and brittle. For example, Bi_2Te_3 thin films can be prepared by mechanical exfoliation, vacuum evaporation, magnetron sputtering, and electrochemical deposition, and subsequently transferred or deposited onto flexible substrates such as polyimide. These processes preserve the established electronic transport characteristics of Bi_2Te_3 while reducing the characteristic length scale associated with bending deformation [52].

However, reducing the thickness of the active layer alone does not guarantee sufficient output performance or long-term cycling stability. Further optimization is therefore required to regulate charge-carrier and phonon transport while preserving the mechanical flexibility of the film. Within the thin-film processing and nanoengineering strategy, established inorganic thermoelectric materials remain among the most mature platforms for practical applications. Their excellent electronic transport properties and relatively high thermal stability have made Bi_2Te_3-based devices important for near-room-temperature waste-heat recovery and wearable thermoelectric applications. Through doping and nanostructural engineering, inorganic semiconductors can partially decouple electrical and thermal transport, thereby achieving a higher thermoelectric figure of merit, ZT. In particular, within the near-room-temperature range (<450 K), Bi_2Te_3-based alloys remain among the most mature electronic thermoelectric systems in terms of both their application base and device development. Their layered structure, relatively low lattice thermal conductivity, and high carrier mobility provide a suitable materials foundation for near-room-temperature thermoelectric conversion. Kim et al. [52] enhanced phonon scattering by introducing dislocation arrays and nanoprecipitates, while dislocations, point defects, and grain boundaries jointly suppressed lattice heat transport and increased ZT . These findings indicate that the flexibility of thin films depends not only on reducing their thickness but also on maintaining sufficient thermoelectric performance in the active material. In comparison, PbTe, SnSe, Cu_2Se, SiGe, and some oxide thermoelectric materials are mainly designed for medium- and high-temperature operation, and their flexibility and suitability for wearable applications are relatively limited. They are therefore not the primary focus of this section.

Once the film thickness and mechanical flexibility have been optimized, compositional regulation and interface engineering can further improve thermoelectric transport and device reliability. Introducing methylammonium lead iodide ($MAPbI_3$) into Bi_2Te_3 films provides a feasible compositional hybridization strategy. Adjusting the Pb/I composition helps optimize carrier transport, whereas the MA-related amorphous phase enhances phonon scattering. As a result, the lattice thermal conductivity decreases from 1.1 to 0.1 $W\,m^{-1}\,K^{-1}$, while the ZT value at 250 °C increases from 0.08 to 0.94. The Young's modulus of the resulting hybrid film decreases markedly, and its resistance changes by only 2.5% after 5000 bending cycles. The corresponding flexible device delivers an output power of 35.3 nW at $\Delta T = 20$ °C [47]. However, compositional hybridization alone cannot fully resolve the interfacial reliability issues between the thermoelectric film and the electrodes. To address this issue, p-type $Bi_{0.5}Sb_{1.5}Te_3$/n-type $Bi_2Te_{2.7}Se_{0.3}$ films were fabricated on a polyimide substrate with a 10 nm Ti contact layer and a 10 nm Ti barrier layer. This interfacial design improves the metal–semiconductor contact and protects the thermoelectric films. The resulting p-type and n-type thermoelectric legs achieve ZT values of 1.39

and 1.44, respectively, while the device reaches a power density of 108 μW cm^{-2} at ΔT = 5 K. After more than 100 bending cycles at a radius of 10 mm, the resistance changes by approximately 3.3% [53]. In addition to interface engineering, doping and defect engineering can relieve bending-induced strain within the crystal structure. For S-doped Bi_2Te_3 films deposited on polyimide, an S content of 3.8% produces a peak power factor of 14.8 μW cm^{-1} K^{-2} at 300 K. S substitution contracts the lattice, weakens the interlayer van der Waals interactions, and promotes strain relaxation through nanoscale slip. Consequently, the resistance change remains below 10% after 1000 bending cycles [54]. These results indicate that flexibility can be introduced not only through flexible substrates and electrode interfaces but also through compositional regulation and crystal-structure design.

When the active phase changes from a continuous film to a network of nanowires or particles, the flexible support must also maintain macroscopic deformability and electrical continuity. Embedding Ag_2Se nanowires in a nylon membrane and establishing continuous electrical pathways through an rGO conductive network represents a typical implementation of this strategy. The flexible support maintains the conductive pathways during deformation, while hot pressing to induce orientation and interfacial energy filtering improve thermoelectric transport. At room temperature, the material achieves a *ZT* value of 1.28 and a power factor of 37 μW cm^{-1} K^{-2}. After 1500 bending cycles at a radius of 5 mm, its electrical conductivity remains at 96.9% of the initial value. An out-of-plane generator containing 100 pairs of thermoelectric legs delivers a power density of 6.7 mW cm^{-2} at ΔT = 26 K [55]. Building on this design, Ag-Ag_2Se-graphene ternary composite films use multiple interfaces to maintain carrier transport during bending. The Ag-Ag_2Se and Ag_2Se-graphene interfaces jointly regulate the carrier concentration and energy-filtering effect. At a graphene content of 0.25 wt%, the $Ag_{2.25}Se$ composite film achieves a power factor of 1643 μW m^{-1} K^{-2}. A flexible device assembled from this film with three thermoelectric legs produces approximately 1.5 μW at ΔT = 50 K and retains good mechanical stability after 800 bending cycles [56]. Taken together, nanoscale transport engineering, multicomponent interfaces, and macroscopic flexible supports can work cooperatively to maintain carrier transport during deformation. Nevertheless, the thin-film strategy involves inherent performance trade-offs. Reducing the thickness and engineering the interfaces can improve bending tolerance and integration, but may also reduce the temperature difference established across the device and increase contact thermal resistance or parasitic heat loss. Thin-film nanoengineering should therefore be coordinated with electrode, substrate, and thermal-boundary design.

Compared with electronic thermoelectric systems, ionic thermoelectric films play a greater role in regulating geometric configuration and ion transport than in achieving flexibility through the active material itself. Reducing the film thickness can shorten ion-diffusion pathways, regulate liquid retention, and facilitate planar encapsulation. Among the ionic systems considered in this section, gels, fibers, and porous networks are generally more suitable for balancing ion transport and mechanical compliance. The evaluation of ionic thermoelectric films should therefore also report key conditions such as relative humidity, film thickness, solvent pretreatment history, and electrode-boundary conditions [57–59].

Overall, thin-film processing and nanoengineering use existing high-performance electronic thermoelectric materials and relatively mature fabrication methods to achieve bending tolerance. Their limitations mainly arise from the trade-offs among film thickness, mechanical flexibility, and device consistency. An excessively thick film increases bending stiffness, whereas an excessively thin film may compromise electrical continuity and long-term stability. In addition, interfacial stresses generated during repeated bending may lead to progressive degradation of device performance.

3.2. Island–bridge architectures for flexibility and strain distribution

Thin-film processing primarily achieves bendability by reducing bending stiffness, but it does not fundamentally improve the tensile capability of the material itself. When a device must withstand stretching or twisting, island–bridge architectures can spatially separate thermoelectric active islands from flexible interconnects: the thermoelectric islands perform energy conversion, while serpentine interconnects and elastic regions accommodate deformation and redistribute strain. Unlike thin-film processing, which emphasizes dimensional control and transport optimization, island–bridge architectures mainly achieve device-level flexibility through strain partitioning. This strategy is therefore particularly suitable for sensor arrays, stretchable interconnects, and textile-integrated devices. In a Bi—Te thermoelectric electronic skin, a 4 × 4 array of rigid thermoelectric islands was chemically bonded to a polydimethylsiloxane substrate and interconnected using flexible serpentine wires, enabling self-powered temperature sensing. The system achieves a sensitivity of 729 μV K^{-1}, a response time of 0.157 s, and a spatial resolution of 2.75 × 2.75 mm^2. Its sensing performance remains largely unchanged under 30% tensile strain, and the device withstands repeated mechanical cycling. Accordingly, the thermoelectric islands retain the voltage output of the inorganic material, whereas the bridge regions and flexible substrate accommodate deformation and redistribute strain [48].

Following the development of local temperature-pixel sensing, stretchable interconnects have further expanded the deformation tolerance of island–bridge devices. Yang et al. connected p-type Sb_2Te_3 and n-type Bi_2Te_3 thermoelectric cubes using wavy serpentine interconnect electrodes and embedded them in an Ecoflex elastomer. The device withstands 50% biaxial stretching, while the internal resistance of its 50 pairs of thermoelectric elements is 22 Ω. When attached to dynamically moving finger and wrist surfaces, the output voltage varies by less than 3%. The device can also power pressure and bending sensors for heart-rate monitoring and gesture recognition [48].

In another structural implementation, Lee et al. [60] replaced rigid copper electrodes with stretchable silver nanowire (AgNW) electrodes and introduced a magnetically self-assembled Ag—Ni particle/PDMS soft thermally conductive composite. The composite has a Young's modulus below 10 MPa and a thermal conductivity of approximately 1.4 W m^{-1} K^{-1}. An array containing 220 pairs of Bi_2Te_3 thermoelectric legs delivers an output power of 7.02 mW and an output voltage of 2.12 V at a temperature difference of 40 K. When the design focus shifted toward textile integration, Hou et al. embedded rigid Bi-Te/Sb-Te thermoelectric cubes into laser-cut openings in an elastic textile and interconnected them using serpentine conductive-fabric electrodes. The device maintains stable output under 30% stretching, with an open-circuit voltage of 111.49 mV at ΔT = 33.24 K and a maximum power of 64.10 μW [61]. These structural developments indicate that island–bridge architectures can progressively expand the stretching capability and integration forms of thermoelectric devices through the coordinated design of interconnects, electrodes, thermal management, and textile carriers.

The island–bridge principle can also be extended to conductive-network design within materials, although this structural concept should be distinguished from thermoelectric functionality. Ding et al. used MXene as the conductive islands and PEDOT:PSS as the connecting bridges to construct a conductive network in a PVA/MXene/PEDOT:PSS hydrogel. The network can fracture and recover under deformation, increases the electrical conductivity by 188% to 21.09 S cm^{-1}, and improves the strain sensitivity by 98% (GF = 2.31), enabling wearable posture monitoring [62]. Because its primary function is to construct a recoverable flexible conductive network rather than to achieve thermoelectric conversion, these results should not be directly compared with thermoelectric output performance. This extension demonstrates that island–bridge structures can be used not only to spatially separate thermoelectric active units from flexible interconnects but also to

regulate conductive pathways within flexible materials.

To date, island–bridge architectures have mainly been applied to electronic thermoelectric devices, and no clear ionic thermoelectric island-bridge system has been established. Ionic thermoelectric materials generally operate as gel or hydrogel networks, in which flexibility arises primarily from the collective deformation of the continuous network rather than from the spatial separation of rigid islands and flexible bridges. Ionic systems are therefore more suitable for flexibility engineering through integration with elastic substrates, gel matrices, and intrinsically stretchable networks. Extending island–bridge architectures to ionic thermoelectric devices will require further consideration of ion-transport continuity, interfacial stability, and gel encapsulation. Overall, island-bridge architectures spatially assign the thermoelectric conversion units and the deformable interconnect and elastic regions to different functional components. This arrangement preserves the output capability of inorganic thermoelectric materials while improving the stretching, twisting, and array-integration capabilities of the device. For self-powered biosensing, the architecture can decouple the local temperature response from the stretchability of the overall device, making it particularly suitable for spatially resolved temperature imaging and local heat-source detection. Nevertheless, the fabrication of island arrays, construction of reliable interfaces, and development of low-resistance interconnects increase manufacturing complexity. Compared with applications requiring only low-cost, large-area coating, island–bridge architectures are more appropriate for flexible thermoelectric sensing platforms that demand high spatial resolution, localized thermal response, and strong mechanical adaptability.

3.3. Integration with elastic substrates and gel matrices

Unlike island-bridge architectures, which transfer strain through spatial separation, elastic-substrate/gel-matrix composites combine thermoelectric components with a soft matrix capable of accommodating macroscopic deformation. The soft matrix can improve conformal contact, bending tolerance, and environmental protection, while its thickness, thermal conductivity, and interfacial state directly affect the temperature difference between the hot and cold sides. Accordingly, evaluating these systems requires consideration not only of the mechanical properties of the matrix but also of the thermoelectric output after compositing, interfacial stability, and performance retention under cyclic deformation. According to their dominant transport mechanisms, the reported systems can be divided into electronic thermoelectric composites governed primarily by charge-carrier transport and ionic gels or ionogel fibers governed primarily by ion migration.

In electronic thermoelectric elastomer composites, conductive polymers are commonly combined with inorganic or carbon-based components to maintain flexibility and continuous electronic transport pathways. Bi_2Te_3/PEDOT nanowire sandwich structures and Te/PEDOT:PSS films are representative configurations. Meanwhile, the mechanical response of the elastic matrix can be regulated through compositional and phase-structure design. PEDOT:PSS/waterborne polyurethane composites exhibit skin-like J-shaped stress–strain behavior, with an elongation exceeding 500% [63]. Molecular and phase-structure regulation can improve conformal contact and deformation tolerance, but a high elongation alone cannot replace thermoelectric performance parameters and must be evaluated together with the Seebeck coefficient, power factor, or device output. Accordingly, the role of the elastic matrix extends beyond accommodating mechanical deformation; it also provides stable interfacial contact and continuous structural support for the thermoelectric active phase.

For electronic thermoelectric systems, the transport properties of conductive polymers such as PEDOT:PSS can be further optimized through acid treatment, solvent engineering, secondary doping, phase separation, and interface control, thereby reducing the potential decrease in electrical conductivity caused by introducing an elastic matrix [64,65]. However, improving electrical conductivity is not the sole objective in flexible thermoelectric sensors. The composite or encapsulation layer must also avoid excessively reducing the temperature gradient within the device. Unlike electronic systems, which mainly rely on the combined action of the conductive phase and elastic matrix to maintain electronic transport, ionic systems depend more strongly on the integrity of the gel network, solvent retention, and ion migration.

Ionic thermoelectric materials therefore generally require gel-network design and fiber formation to simultaneously satisfy the requirements of mechanical compliance and ion transport. Organic–inorganic hybrid ionogel fibers illustrate the development of ionic thermoelectric gels into flexible and weavable carriers. For the PVDF-HFP/EMIM:DCA/NaTFSI/SiO_2 system, antisolvent treatment, doping, and hybridization strategies can be used to regulate crystallinity, ion dissociation, and ion migration. The optimized ionogel film exhibits an ionic Seebeck coefficient of 47.5 mV K^{-1}, an ionic conductivity of 43.7 mS cm^{-1}, and an ionic power factor of 9845.8 μW m^{-1} K^{-2}. After being coated onto cotton-based fibers, the tensile strength and elongation of the fibers increase to 17.7 MPa and 70%, respectively, while an ionic Seebeck coefficient of approximately 44.27 mV K^{-1} is retained [49]. These results indicate that a fiber carrier can not only improve the mechanical load-bearing capacity of the ionogel but also preserve its relatively strong ionic thermoelectric response.

Overall, elastic substrates and gel matrices provide a common integration pathway for introducing flexibility into electronic and ionic thermoelectric materials by offering soft support, improving interfacial contact, and maintaining structural integrity. Electronic composites mainly require coordinated regulation of conductive-network continuity, interfacial stability, and the influence of the elastic matrix on the temperature gradient. Ionic systems place greater emphasis on the balance among gel-network integrity, solvent retention, and ion migration. Therefore, the evaluation of these flexible thermoelectric systems should encompass mechanical deformability, thermoelectric transport, interfacial reliability, and long-term cycling stability.

3.4. Intrinsically stretchable designs

Unlike elastomer composite strategies that rely on a soft matrix to accommodate deformation, intrinsically stretchable designs use molecular network construction or phase-separated structures to make the thermoelectric active material itself stretchable, thereby reducing its dependence on external matrices and complex interconnect architectures. For electronic thermoelectric elastomers, methods such as nanoscale phase separation, thermally triggered crosslinking, and oriented n-type doping can introduce stretchability into the material network. The resulting material exhibits a ZT of 0.49 at 300 K, can be stretched by more than 850%, and maintains an elastic recovery of more than 90% at 150% strain [50]. Accordingly, the elastomer does not function merely as a passive encapsulation layer; its molecular network can also contribute to the coordinated design of mechanical properties and electronic transport. However, the flexibility of electronic systems mainly relies on continuous conductive networks to maintain electronic transport. When mobile ions become the carriers involved in heat transport between the hot and cold sides, the material must additionally address ion dissociation, ion diffusion, and solvent retention.

In ionic thermoelectric systems, the thermodiffusion of cations and anions jointly generates thermovoltage. Because the ionic Seebeck coefficients of ionic materials are generally expressed in mV K^{-1}, whereas the Seebeck coefficients of electronic thermoelectric materials are typically on the order of μV K^{-1}, the two types of systems should be evaluated separately according to their respective mechanisms and testing conditions. A graphene oxide-modified acrylamide ionic gel exhibits an ionic power factor of 753.0 μW m^{-1} K^{-2} and *ZT* of 0.19, an elongation of 389%, and a tensile strength of 219.7 kPa. An integrated device comprising nine thermoelectric legs achieves a maximum power density of 1.32 mW cm^{-2} at $\Delta T = 20$ K. A hydrophilic three-dimensional network can provide continuous pathways for ion migration under

substantial deformation. Meanwhile, a PVA-based n-type ionic thermoelectric hydrogel uses the synergistic effects of Cu^{2+} coordination and the hydrophobic association of PMNT chains to achieve an ionic Seebeck coefficient of −38.6 mV K^{-1}, a stretchability of 382.5%, and a *ZT* of 0.01. Its self-powered temperature array exhibits a sensitivity of approximately 36 mV K^{-1} [66,67]. These parameters reflect the ability of ionic thermoelectric networks to maintain both ion transport and thermoelectric output under substantial deformation.

The network structure of ionic gels affects both mechanical integrity and ion transport. Physical crosslinks, including hydrogen bonding, electrostatic interactions, and hydrophobic association, can impart biocompatibility or self-healing capability, whereas chemical crosslinking helps improve network stability and mechanical strength [57]. Combining physical and chemical crosslinking can enhance stretchability and toughness while maintaining ionic conductivity. For temperature sensing, an ionic thermoelectric sensor based on a fluoroelastomer/ionic liquid can distinguish temperature gradients as small as 0.01 K, with a temperature resolution of approximately 0.001 K [63]. Building on this principle, ion-selective coordination can further modify the relative migration of cations and anions, thereby regulating the direction of ion thermodiffusion. PEO-based ionic gels illustrate how coordination interactions and phase-separated structures regulate ionic thermoelectric responses and self-healing behavior. In n-type ionic thermoelectric materials, a ternary PEO/LiTFSI/EmimBF₄ ionic gel uses coordination between Li^{+} and the ether oxygen groups of PEO to form ion-selective associations and promote anion-dominated transport. At a relative humidity of 50%, it exhibits an ionic Seebeck coefficient of −15 mV K^{-1} and an ionic conductivity of 1.86 mS cm^{-1}, together with rapid self-healing and recyclability [67]. By contrast, a self-healing PEO/LiTFSI/EmimCl ionic gel uses metal–halogen interactions to induce phase separation and regulate the differences between cation and anion migration. Across different compositions, its ionic Seebeck coefficient ranges from approximately −4 to 13 mV K^{-1}. The optimized formulation exhibits an ionic Seebeck coefficient of approximately 14 mV K^{-1}, an ionic conductivity of 4.8 mS cm^{-1}, and a power factor of 97.3 μW m^{-1} K^{-2}. The material can be stretched to 2000% and retains an ionic Seebeck coefficient of 13.1 mV K^{-1} after cutting and self-healing [68]. In addition, a supramolecular hydrogel constructs a recoverable ionic network through host–guest interactions, hydrogen bonding, and electrostatic interactions. It exhibits a tensile strain of 2173%, a strength of 340 kPa, a toughness of 2.88 MJ m^{-3}, and a p-type ionic Seebeck coefficient of 2.95 mV K^{-1}. The corresponding modular ionic thermoelectric capacitor produces a thermovoltage output of up to 14.3 mV K^{-1}. The material has an ionic conductivity of 18.19 mS cm^{-1} and also exhibits self-healing and adhesive properties [69]. Taken together, ion-selective coordination, phase separation, and reversible molecular interactions can cooperatively regulate ion migration, mechanical recovery, and thermoelectric response at different levels.

Overall, intrinsically stretchable designs enable thermoelectric active materials to accommodate mechanical deformation themselves, thereby reducing the risk of mismatch between the active phase and the external matrix. For electronic systems, nanoscale phase separation, crosslinking, and doping are mainly used to maintain continuous electronic transport. For ionic systems, gel networks, ion-selective coordination, solvent retention, and reversible molecular interactions jointly determine mechanical flexibility and thermoelectric response. Molecular network design can further impart functions such as self-healing and adhesion, providing additional options for biointegrated sensing. Nevertheless, the practical advantages of these materials still need to be comprehensively evaluated in terms of thermoelectric output, cycling durability, mechanical recovery, and environmental stability.

3.5. *Fiber, textile, and 3D porous architectures for flexibility*

Intrinsically stretchable designs enable materials to accommodate mechanical deformation themselves, but they often rely on specific molecular structures or phase-separated conditions, which remain challenging for large-area continuous processing. By contrast, fibers, yarns, textiles, porous networks, and three-dimensional soft architectures can achieve flexibility through geometric deformation, load distribution, and the incorporation of air or elastomer regions. They can also be further fabricated into breathable and conformal forms suitable for weaving, knitting, embroidery, or printing. Unlike strategies that rely on an elastic matrix to directly accommodate deformation, these systems use the fiber and porous architectures themselves to distribute mechanical loads, regulate heat flow, and adapt to wearable form factors. A representative PEDOT:PSS/Te@PANI ternary composite fiber introduces a PANI interlayer between the Te nanowires and PEDOT:PSS, while establishing interfacial interactions such as Te—N coordination bonds, hydrogen bonding, and π–π stacking. The composite fiber exhibits a power factor of 552.9 μW m^{-1} K^{-2}, a tensile strength of 355 MPa, and a fracture strain of 26%. Its electrical conductivity retention remains above 95% after 1000 bending cycles [70]. Accordingly, dual-interface engineering improves the thermoelectric transport and mechanical durability of the fiber primarily by enhancing the interfacial stability between the inorganic nanowires and the conductive polymer phase.

Unlike composite fibers that rely on interfacial engineering, carbon nanotube thermoelectric yarns depend more strongly on continuous carbon networks and macroscopic twisting to maintain transport pathways. After chemical modification and mechanical twisting, their maximum power factor reaches 953 μW m^{-1} K^{-2} [71]. In this system, the focus of flexibilization shifts from microscopic interfacial stability toward continuous conductive networks and weavable structures at the yarn scale. Yarns provide continuous one-dimensional transport pathways, whereas textile architectures further determine the coverage, interconnection, and skin contact of the thermoelectric units. Therefore, performance evaluation must extend from individual yarns to the temperature response and deformation tolerance of the textile. A representative three-dimensional flexible thermoelectric textile exhibits a temperature resolution of approximately 0.02 K and a response time of approximately 240 ms, while maintaining thermoelectric output at a strain of approximately 50% [72]. These results indicate that transport continuity at the fiber scale must be further translated into stable temperature responses over large-area textile devices.

Building on the large-area coverage and mechanical decoupling provided by textile structures, fiber composites can further improve environmental durability and system-level output. PEDOT:PSS/SWCNT@PU composite fibers are prepared by freeze–thaw-assisted wet spinning and exhibit an electrical conductivity of 1960 S cm^{-1}, a power factor of 59.6 μW m^{-1} K^{-2}, and a tensile strength of 103 MPa. Polyurethane encapsulation improves their resistance to bending, twisting, washing, and low-temperature environments. A thermoelectric textile comprising 32 pairs of p-type thermoelectric legs achieves a power density of 60.1 μW cm^{-2} at $\Delta T = 50$ K and retains more than 95% of its performance after mechanical deformation [51]. In addition, the PEDOT:PSS/SWCNT@PU core–shell composite fibers exhibit good environmental durability. After continuous stirring in water for 30 days, the decreases in electrical conductivity and Seebeck coefficient are both less than 2%. Their thermoelectric performance also remains stable after storage at −18 °C for 30 days [49]. These results indicate that fiber-level thermoelectric properties can be translated into stable system-level output only after textile assembly and appropriate thermal management are considered.

For devices operating under large temperature differences or requiring tolerance to localized damage and complex thermal management, simply increasing the number of fibers may not provide the most effective performance improvement. In such situations, three-dimensional soft architectures can complement fiber- and textile-based structures by providing spatial thermal insulation and repairable interconnections. One study used three-dimensional printing to integrate multifunctional elastomers, self-healing liquid-metal conductors, and

Table 1-1
Representative thermoelectric and sensor/system performance metrics of flexible thermoelectric sensors in biosensing.

Material system	Key metrics	Application	Ref.
Graphene fiber/Pt thermocouple	S = 29.9 μV/°C	Body temperature (electronic)	[74]
PVA/gelatin+Fe^{2+}/Fe^{3+} patch	Stretch ratio > 2.1	Body temperature (ionic)	[75]
n-type thermoelectric elastomer	ZT = 0.49	Electronic skin (electronic)	[50]
GO/PAM/BMIM ionic gel	S = -76.7 mV K^{-1}	Electronic skin (ionic)	[76]
Bi_2Te_3/Ecoflex TEG	Output power ≈ 170 μW	Sweat (electronic)	[77]
Double-network thermoelectric hydrogel	S = 2.04 mV K^{-1}	Sweat (ionic)	[78]
Te/CuTe IR detector	Temperature resolution = 0.05 °C; response time = 154 ms	Robotic thermal nociception (electronic)	[79]
Thermogalvanic hydrogel array	S = 1.57 mV K^{-1}; recognition accuracy = 98.8%	Robotic thermal sensing (ionic)	[80]
Photo-induced p-n integrated thermoelectric	Temporal variation<1%; spatial variation = 4.54%; accuracy> 98.6%	Robotic thermal nociception (electronic)	[81]

Note: "S" denotes the Seebeck coefficient. For ionic systems, S is reported as the ionic Seebeck coefficient in mV K^{-1}. The listed metrics distinguish thermoelectric performance from sensor/system-level performance and are not intended for direct ranking across electronic and ionic systems.

rigid thermoelectric semiconductors into a single device. The device operates at strains of up to 230% and achieves a power density of 115.4 μW cm^{-2} at ΔT = 10 °C. It retains its functionality after repeated puncture damage and 2000 stretching cycles at 50% strain. Porous or thermally insulating three-dimensional structures can reduce device weight and help maintain the temperature gradient across the thermoelectric legs [73]. This 3D-printed structure achieves deformability mainly through the combined effects of the soft matrix, liquid-metal interconnects, and rigid thermoelectric phase. Further co-design of the thermoelectric leg dimensions, interconnect geometry, and radiative cooling layer may improve the output per unit area while maintaining stretchability.

Overall, fibers, textiles, and three-dimensional porous structures provide a route to flexible thermoelectric materials that is relatively independent of the intrinsic mechanical properties of the materials. Through geometric design, these systems can distribute loads, regulate heat flow, and adapt to wearable form factors. An important advantage is that the thermoelectric active material itself does not need to be intrinsically stretchable. This route can also be combined with thin-film processing, elastomer composites, or intrinsically stretchable designs to establish multilevel flexibility strategies. However, its performance is affected by the coupled relationships among electrical interconnections, thermal resistance, breathability, and mechanical fatigue. Increasing porosity can improve softness and thermal insulation but may reduce the number of effective transport pathways. Increasing the thermoelectric phase content can enhance power output but may compromise stretchability and washability.

Taken together, the five flexibility strategies show that flexibility is not an intrinsic property of a particular class of materials; instead, it is a combined characteristic governed by dimensions, interfaces, matrices, and structures. Thin film processing and nanoengineering use established electronic thermoelectric materials to achieve bending tolerance. Island–bridge architectures improve device level strain tolerance through strain distribution. Elastic substrates and gel matrices provide soft support or continuous ionic networks for electronic and ionic systems, respectively. Intrinsically stretchable designs enable the active materials themselves to accommodate deformation. Fibers, textiles, and 3D porous structures use geometric design to enable lightweight, breathable wearable integration.

In terms of carrier type, the electronic materials discussed in this section are found mainly in thin films, island–bridge devices, and fiber or textile systems. Their design priorities include electronic transport, power factor, and electrical continuity under cyclic deformation. Ionic materials appear more often in ionic gels, fibers, and intrinsically stretchable networks, for which key metrics include the ionic Seebeck coefficient, ionic conductivity, solvent retention, and self-healing capability. The two classes of systems operate through different transport mechanisms, so their performance metrics should be interpreted in relation to the application scenario and test conditions.

4. Applications of flexible thermoelectric sensors in biosensing

The mechanisms and flexibility strategies discussed above determine how electronic and ionic thermoelectric materials can be integrated into biosensing platforms, but their practical value depends on application-specific requirements such as skin conformability, available temperature gradients, and signal compatibility. Because these requirements vary considerably across studies, a consolidated comparison is useful for clarifying the roles of different material systems. To provide a common reference for the following case discussions, Table 1-1 summarizes representative flexible thermoelectric sensors in biosensing, listing their material systems, key performance metrics, and application functions. This overview provides a common reference for the following case discussions, where electronic and ionic systems are distinguished according to their reported functions rather than ranked by a single metric.

4.1. Applications in body temperature monitoring

The preceding sections introduced the operating principles, mechanisms, and material systems of thermoelectric sensors. Building on the material classification established in above, this section discusses how electronic-type and ionic-type thermoelectric materials contribute differently to body-temperature monitoring. In the fields of flexible electronics and wearable healthcare, how to design thermoelectric materials and device architectures that combine high sensitivity, excellent flexibility, and compatibility with the human body remains a central research issue. In flexible biosensing, the development of temperature sensors with high sensitivity, outstanding mechanical flexibility, and biocompatibility plays an important role in enabling real-time body-temperature monitoring.

4.1.1. Applications of electronic thermoelectric materials in body temperature monitoring

Electronic-type thermoelectric materials, such as graphene fibers, carbon nanomaterials, and inorganic BiTe-based pillars, rely on charge-carrier transport and typically exhibit high Seebeck coefficients and good long-term stability, making them suitable for precise body-temperature monitoring. In the development of highly sensitive flexible body-temperature sensors, Wang et al. proposed a flexible thermoelectric temperature sensor based on graphene fibers (GFs), demonstrating the considerable potential of novel thermoelectric carbon-based nanomaterials for applications in wearable electronic skin [74]. This study was aimed at overcoming the limitations of conventional thermocouples, which are inherently rigid and therefore difficult to conform to the curved surfaces of human skin. From a theoretical perspective, the sensor exploits the excellent charge-transport properties of graphene and optimizes the Seebeck coefficient by regulating the material's Fermi level. For sensor fabrication, the researchers employed the prepared graphene fibers (GFs) as the anode (p-type thermoelectric material) and platinum wire (Pt) as the cathode. These components were connected using conductive silver paste and encapsulated on a flexible polyimide (PI) substrate, thereby forming a thermocouple structure with distinct hot and cold junctions. The sensor operates based on the Seebeck effect, whereby the temperature difference (ΔT) between the hot junction and the cold junction drives charge-carrier diffusion,

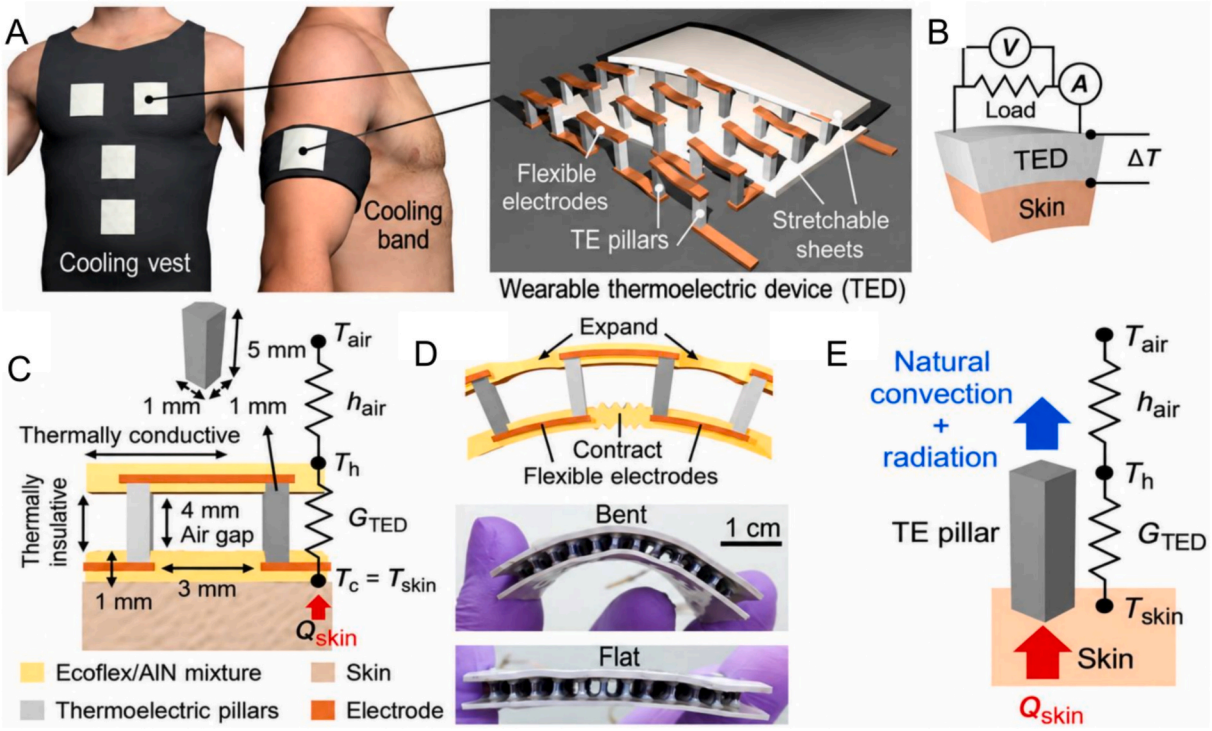


Fig. 5. Structural Configuration and Operating Mechanisms of the Flexible Thermoelectric Device (TED). (A) Schematic illustration of the overall structure of the TED. (B) Human body surface thermal-energy harvesting test system. (C) Internal thermal-management structure design of the TED. (D) Demonstration of the device's mechanical flexibility and bending capability. (E) Power-generation mode based on the Seebeck effect and cooling mode based on the Peltier effect. (A-E) Reproduced with permission from Ref. [82],licensed under CCBY-NC 4.0. Copyright 2019.

generating a thermoelectric voltage (V). Its sensitivity, expressed as the Seebeck coefficient (S), is defined by the following equation:

$$S = \frac{dv}{d\Delta T}$$

To obtain high-performance graphene fibers, the research team employed a simple microfluidic spinning technique and introduced vitamin C as a green reducing agent. This approach simultaneously removed oxygen-containing functional groups from graphene oxide and restored its conjugated structure. This reduction strategy significantly enhanced the electrical conductivity of the fibers. When the vitamin C content was optimized to 2 wt%, the thermocouple composed of graphene fibers and platinum wire exhibited the best thermoelectric performance, achieving a sensitivity as high as 29.9 μV/°C.

In practical biosensing applications, devices must withstand repeated human motion. This sensor demonstrated excellent mechanical flexibility, with the graphene fibers remaining intact without fracture even when tied into a knot. After 1000 bending cycles at different bending angles (30°, 60°, and 90°), the sensor's sensitivity remained essentially unchanged, demonstrating excellent resistance to bending-induced interference. This mechanical robustness enables it to be woven into textiles and conform closely to the skin, allowing real-time and accurate monitoring of human body temperature. Furthermore, after being stored in air for 40 days, the encapsulated sensor retained more than 95.66% of its original sensitivity, demonstrating excellent long-term stability.

However, to achieve more sophisticated body-temperature management and monitoring, relying solely on a single sensing fiber is often insufficient to mitigate thermal interference from the surrounding environment. It is also necessary to consider the device's thermal design at the macroscopic scale, as well as its conformability and adhesion to the skin. Hong et al. [82] proposed a more systematic structural design strategy and developed a flexible thermoelectric device (TED) for personalized thermal regulation. To demonstrate the adaptability of the flexible thermoelectric device to various body regions, the researchers designed two wearable configurations, such as a cooling vest and a cooling armband (Fig. 5A). The underlying principle of the power-generation testing, shown in Fig. 5B, relies on the temperature difference established between human skin and the surrounding environment to drive thermoelectric conversion. To enhance the utilization efficiency of this temperature gradient, an internal air-layer structure was incorporated into the TED design (Fig. 5C), which effectively suppresses parasitic heat conduction. From a fabrication perspective, the team adopted a double-layer elastomer architecture, sandwiching high-performance rigid inorganic thermoelectric pillars (based on BiTe materials) between two stretchable Ecoflex films, while intentionally retaining an insulating air layer between them to minimize thermal losses.

This unique “sandwich” architecture reduces the bending stiffness by approximately 70% compared with conventional single-layer designs. As shown in Fig. 5D, the double-layer elastomer configuration enables the device to release mechanical stress during bending, thereby significantly enhancing its flexibility and wearing comfort while improving the overall mechanical adaptability of the TED. During bending, the upper stretchable layer expands while the lower stretchable layer contracts, allowing the device to conform closely to the surface of human skin without compromising wearing comfort. This structural design elegantly overcomes the longstanding challenge that conventional rigid thermoelectric devices cannot achieve intimate contact with the skin. At the same time, the use of thermoelectric pillars with a high aspect ratio effectively reduces heat leakage. Fig. 5E further illustrates the process by which heat is dissipated through natural convection and thermal radiation, which constitutes an important foundation for the efficient thermal management achieved by the TED. As shown in Fig. 5E, the device integrates the Seebeck effect and the Peltier effect into a single system. It first generates electrical power through the Seebeck effect and then utilizes its unique structural design to achieve cooling via the Peltier effect. Consequently, at the application level, the device not only

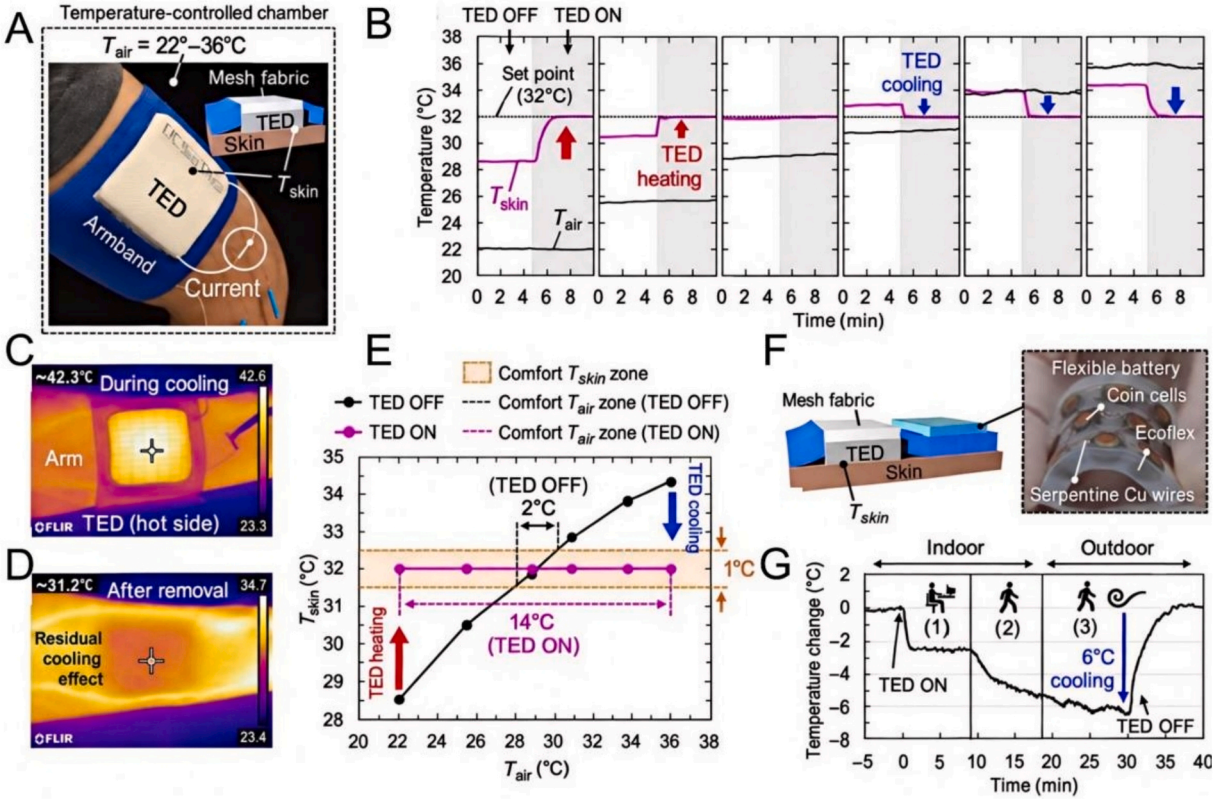


Fig. 6. Validation of the Human Body Temperature Regulation Performance of the Flexible Thermoelectric Device (TED). (A) Schematic illustration of the TED armband structure and experimental setup. (B) Regulation of skin temperature by the TED under different ambient-temperature conditions. (C) Infrared thermal image of the hot-side region during device operation;
(D) Skin-surface temperature distribution after removal of the device. (E) Expansion of the human thermal comfort range enabled by the TED. (F) Integrated system consisting of the TED and a flexible battery. (G) Comparison of skin-cooling performance under different activity conditions . (A-G) Reproduced with permission from Ref. [82], licensed under CCBY-NC 4.0. Copyright 2019.

demonstrates a powerful active-cooling capability, achieving a temperature reduction of more than 10 °C, but also possesses the ability to harvest thermal energy from the surface of the human body. This device is not only a thermal-regulation actuator but also an efficient energy-conversion interface capable of sensing the temperature difference between the skin and the surrounding environment. It provides a solid hardware foundation for future closed-loop health management systems that integrate body-temperature monitoring, energy harvesting, and active thermal regulation into a single platform.

Building upon its outstanding thermal-regulation capability and mechanical flexibility, this technology exhibits broad application prospects in the healthcare and medical fields. Its core advantage lies in its ability to deliver precise thermal doses to specific regions of the body, thereby enabling targeted physical therapy and symptom management. In clinical pathological intervention, this technology provides a novel adjunctive therapeutic approach for patients with multiple sclerosis (MS) and other neurological disorders, alleviating neurological symptoms through localized thermal management. Beyond direct medical intervention, this technology also holds significant value in preventive medicine and occupational health protection. It is particularly well suited for individuals who are required to remain in high-temperature environments for extended periods, such as firefighters, construction workers, and outdoor athletes. By providing effective thermal regulation, the device can help prevent heat stress, heatstroke, and thermal injuries, thereby offering critical thermal protection in demanding environments. To validate the practical effectiveness of the TED in human thermal management, Hong et al. further conducted wearable human-subject experiments, the results of which are presented in Fig. 6 [82]. To comprehensively evaluate the practical thermal-regulation performance of the flexible thermoelectric device (TED), the research team conducted wearable experiments on human participants. In the experimental setup, subjects wore a TED armband while their skin surface temperature was monitored in real time (Fig. 6A). The results showed that when the TED was switched off, skin temperature fluctuated significantly with changes in ambient temperature; however, once the TED was activated, skin temperature was consistently maintained at approximately 32 °C, demonstrating precise temperature regulation capability (Fig. 6B). During the cooling process, infrared thermal imaging further revealed that heat could be rapidly transferred from the skin surface to the surrounding environment (Fig. 6C). Notably, even after the TED was removed, a discernible residual cooling effect remained on the skin surface, indicating that the device possesses sustained thermal-management characteristics (Fig. 6D). Furthermore, the study quantified the impact of the TED on human thermal comfort and found that it could expand the comfortable ambient temperature range from approximately 2 °C to 14 °C, significantly enhancing the wearer's adaptability to varying environmental conditions (Fig. 6E). In terms of wearable practicality, the integrated design of the TED with a flexible battery system was also validated, confirming its potential for mobile and wearable applications (Fig. 6F). Finally, the researchers verified the cooling performance of the device across multiple real-world scenarios, including indoor sitting, indoor walking, and outdoor exercise. In all cases, the TED achieved a maximum temperature reduction of 6 °C, fully demonstrating its effectiveness and broad applicability in personal thermal management (Fig. 6G).

In summary, by integrating a proportional-integral-derivative (PID) control algorithm, the flexible thermoelectric device is capable of precisely maintaining skin temperature at the physiologically comfortable

set point of 32 °C, even under substantial fluctuations in ambient temperature (varying between 22 °C and 36 °C). As a result, it significantly broadens the range of environmental conditions to which the human body can comfortably adapt. Furthermore, through integration with a flexible battery system, the technology successfully eliminates dependence on fixed external power sources, demonstrating its feasibility as a mobile healthcare device capable of continuously monitoring and regulating body temperature in everyday settings. Flexible thermoelectric body-temperature sensors have evolved from simple single-point temperature detection devices into integrated systems that combine energy harvesting, body-temperature monitoring, and thermal regulation. Future research efforts will primarily focus on enhancing power output, long-term operational stability, and system-level integration capabilities.

Otherwise , Luo et al. [51] developed continuous PEDOT:PSS/SWCNT@PU core–shell composite fibers using a wet spinning process assisted by freeze thaw induced gelation. The resulting fibers exhibited an electrical conductivity of 1960 S cm^{-1}, a power factor of 59.6 μW m^{-1} K^{-2}, and a breaking strength of 103 MPa. The PU encapsulation layer provided excellent weavability and washability, with less than 2% degradation in both electrical conductivity and Seebeck coefficient after continuous stirring in water for 30 days. The thermoelectric performance also remained stable after storage at −18 °C for 30 days. A thermoelectric textile comprising 32 pairs of p-type legs achieved a power density of 60.1 μW cm^{-2} under a temperature difference of 50 K and retained more than 95% of its initial performance after 1000 cycles of bending, twisting, stretching, and rubbing. When integrated into an intelligent body temperature monitoring and alarm system, the textile provided warning responses within 5 s for both low grade and high-grade fever. Combined with a convolutional neural network algorithm, the system achieved an accuracy of 94% in classifying body temperature states [51].

In summary, electronic-type thermoelectric materials for body-temperature monitoring are characterized by high Seebeck coefficients, high power factors, and excellent long-term stability. Their charge-carrier-dominated transport enables precise temperature-to-voltage conversion, as demonstrated by graphene-fiber thermocouples and BiTe-based flexible TEDs. However, their intrinsic rigidity or limited stretchability often requires structural engineering, such as double-layer elastomer architectures and air-layer thermal isolation, to achieve conformal skin contact. These materials are therefore most suitable for applications requiring high sensing accuracy, stable output, and active thermal regulation.

4.1.2. Applications of ionic thermoelectric materials in body temperature monitoring

In contrast to electronic-type materials, ionic-type thermoelectric materials rely on thermally induced ion migration and exhibit exceptionally high thermovoltages, excellent stretchability, and intrinsic biocompatibility, making them attractive for skin-conformal body-temperature monitoring. The graphene fiber/Pt thermocouple described above relies on electrons or holes migrating under a temperature gradient to convert the temperature difference between the skin and the surrounding environment into a voltage signal. For body-temperature monitoring, the main limitation on output is often the small magnitude of this temperature difference, which is typically only a few kelvin, rather than the absence of a temperature gradient. The device must also maintain stable contact during bending, conformal attachment, and body movement. While retaining the direct electrical readout of electronic thermoelectric devices, researchers have therefore begun to extend the range of charge carriers to include ions, enabling the flexible interface itself to mediate ion transport and temperature sensing. For example , Zhang et al. [75] combined a PVA/gelatin double-network gel with a Fe^{2+}/Fe^{3+} redox couple and used MWCNT/PDMS composite electrodes for flexible encapsulation, creating a thermoelectrochemical patch for body-temperature and pulse monitoring. Hydrogen bonding and physical entanglement in the double-network structure improved the gel's tolerance to deformation. The device withstood stretch ratios exceeding 2.1, had a tensile strength of approximately 0.4 MPa, and maintained stable output over 50 cycles. During operation, a temperature difference drives reversible redox reactions of Fe^{2+}/Fe^{3+} at the electrode interfaces, generating a thermoelectrochemical voltage. Periodic changes in contact and pressure caused by the wrist pulse are simultaneously read out as a current signal. When attached to the wrist, the device tracked simulated changes in body temperature and distinguished pulse rates of approximately 78 and 102 beats min^{-1} before and after exercise. These results show that an ionic thermoelectric gel can integrate temperature sensing and physiological mechanical signals within a single flexible interface.

As monitoring expands from single-point patches to wearable textiles, devices must also combine continuous fiber length with breathability and weavability. Li et al. used PVDF-HFP as the polymer backbone and incorporated EMIM, NaTFSI, and SiO_2 to produce an organic/inorganic hybrid ionic gel fiber. After coating cotton yarn, the fiber's tensile strength and fracture strain increased to 17.7 MPa and 70%, respectively, while retaining its ionic thermoelectric response. At 90% relative humidity, its ionic Seebeck coefficient was 47.5 mV K^{-1}, its ionic conductivity was 43.7 mS cm^{-1}, and its ionic power factor reached 9845.8 μW m^{-1} K^{-2}. The researchers then knitted 10 p-type units into a wearable device. With a temperature difference of approximately 2.6 K between the arm and the environment, the device generated an output voltage of approximately 284 mV, demonstrating the potential of fiber-based ionic thermoelectric materials for harvesting body heat under small temperature differences and for skin-contact temperature monitoring [49].

In efforts to combine p-type and n-type responses in ionic thermoelectric devices, Yu et al. constructed an n-type ionic thermoelectric hydrogel based on PVA-$CuCl_2$-PMNT through hydrophobic and coordination interactions. The hydrogel had an ionic Seebeck coefficient of −38.6 mV K^{-1} and a stretchability of 382.5%. When fabricated into a 6 × 6 array and attached to a prosthetic hand, it spatially mapped the temperature distribution during contact. This example highlights the complementary role of ionic thermoelectric hydrogels: their high thermovoltage and soft array form enable interfacial temperatures to be amplified and spatially resolved under small temperature differences, complementing electronic thermoelectric materials [66].

Overall, electronic and ionic thermoelectric materials offer complementary advantages for body-temperature monitoring. Electronic thermoelectric materials are suited to stable electrical signal output, series-connected thermoelectric legs, and interfaces with downstream circuitry. Their millisecond-scale response makes them suitable for tracking dynamic temperature fluctuations associated with breathing and pulse. Ionic thermoelectric materials are well suited to soft, stretchable, skin-conformal interfaces that generate high thermovoltages. They can amplify small temperature differences at the body surface and show promise for precise measurement of steady-state skin temperature. This division of roles reflects the intrinsic differences in their physical mechanisms rather than a simple ranking of performance.

4.2. Applications in electronic skin

4.2.1. Applications of electronic thermoelectric materials in electronic skin

With the deep integration of artificial intelligence and wearable technologies, future electronic skin (*E*-skin) systems must possess the capability to simultaneously capture multidimensional physiological signals, including body temperature and tactile stimuli. Human skin not only serves as a natural barrier that protects the body from external insults but also functions as a highly sophisticated and coordinated sensory system. As a biomimetic replica of human skin, the functional scope of electronic skin (E-skin) has extended far beyond that of natural skin. In addition to accurately mimicking fundamental sensing functions such as pressure and temperature perception, it has expanded to include

the detection of physical stimuli such as light, sound, magnetic fields, velocity, and acceleration [83,84], thereby enabling a wide range of applications across diverse scenarios. Among the five fundamental human senses—vision, hearing, touch, taste, and smell—touch is the most fundamental and indispensable. Its essence lies in the precise perception of a variety of physical stimuli, among which the detection of pressure, temperature, and humidity is particularly critical [85]. Accordingly, the ability to accurately sense these parameters constitutes a key indicator of the performance and sophistication of electronic skin systems. By integrating pressure- and temperature-sensing capabilities, electronic skin can perform fundamental tasks such as object recognition and hot–cold perception, while also enabling rapid responses in emergency situations. Consequently, it possesses irreplaceable application value in a wide range of fields, including smart wearables [86], soft robotics [87], and human–machine interaction.

In the development of multimodal sensing systems for electronic skin, the effective decoupling of different sensing signals while maintaining their coordinated operation represents a major technical challenge. To address this issue, Tian et al. [88] proposed a thermoelectric-material integration strategy based on Different Electrical Output Signals (DEOS), which provides an efficient solution for multimodal signal discrimination and integration [89].To overcome this challenge, the Different Electrical Output Signals (DEOS) strategy based on the thermoelectric effect has demonstrated unique advantages in signal decoupling. This approach originates from the fundamental physical mechanisms of sensing, utilizing the Seebeck effect to convert temperature gradients into voltage signals, while converting mechanical pressure into variations in resistance or capacitance. This mutually independent dual-channel output mode effectively eliminates signal interference and removes the need for complex backend signal-processing algorithms.

Although multimodal sensing can be achieved in principle, electronic skin must still withstand highly complex dynamic mechanical environments in practical applications, including frequent joint bending and external mechanical impacts when attached to the human body. Conventional inorganic thermoelectric thin films are inherently limited by their brittleness and are therefore highly susceptible to fracture and failure under such high-strain conditions. To improve the biomechanical compatibility of thermoelectric devices, Karthikeyan et al. proposed an innovative solution based on a three-dimensional glassy-carbon microlattice architecture, which substantially enhanced the biomechanical compatibility of the device [90] . In this study, a high-toughness glassy-carbon microlattice was employed as the structural framework. While preserving the thermoelectric energy-conversion functionality, this architecture endowed the device with the ability to withstand compressive strains exceeding 50% and achieve an exceptionally high specific energy absorption capacity. This unique architecture enables the thermoelectric device to conform closely to the wrist, joints, and other body regions much like a second skin. Even during vigorous body movements or accidental impacts, the device can maintain its structural integrity and continuously harvest thermal energy from the body surface in a stable manner, thereby providing a reliable, maintenance-free platform for around-the-clock physiological monitoring.

However, regardless of whether multilayer material stacking or three-dimensional structural buffering is employed, it remains difficult to simultaneously optimize mechanical elasticity and thermoelectric performance. The emergence of n-type thermoelectric elastomers (TEEs) has provided an innovative solution to this longstanding challenge. Liu et al. proposed an ingenious three-dimensional synergistic design strategy. By using Hansen solubility parameters to identify highly compatible elastomers (such as SEBS or IBR), and combining thermally activated crosslinking with targeted doping (N-DMBI), they constructed a homogeneous bulk nanophase-separated structure within the material. This structure consists of an interpenetrating network of conjugated polymer nanofibers, an elastic matrix, and a crosslinked framework, all intricately interconnected throughout the material [50]. This architecture enables the material to maintain intimate contact with the skin even under repeated deformation induced by human movement, thereby providing a stable foundation for continuous energy harvesting and reliable signal sensing.

Benefiting from this reconfiguration of the microstructure, TEEs achieve a qualitative leap in mechanical compliance. Unlike conventional conjugated polymers, which tend to develop microcracks under tensile deformation, TEEs can dissipate mechanical stress through the directional rearrangement of polymer chains during stretching. For example, the thermally activated crosslinked c-N1/SEBS composite can withstand an extraordinary 850% tensile strain. Likewise, the c-N2/IBR material not only maintains an elastic recovery rate exceeding 90% under a large strain of 150%, but also limits its energy loss to less than 25%. Combined with an elastic modulus below 100 MPa, these materials closely match the mechanical properties of human epidermal tissue, enabling them to seamlessly accommodate the 5–50% deformation associated with daily movements of body regions such as the elbow and wrist [8,91,92]. As a result, they offer an almost imperceptible wearing experience. More importantly, this exceptional elasticity is achieved without sacrificing thermoelectric energy-conversion performance.

Bismuth telluride Bi_2Te_3-based materials exhibit enhanced thermoelectric performance at room temperature together with excellent flexibility, and have therefore been widely employed in the fabrication of flexible thermoelectric generators (TEGs) [88,93]. In addition, intrinsically stretchable thermoelectric materials have also been developed. Among them, TEE-2 achieves a *ZT* value of 0.49 at 300 K, representing one of the highest values reported for organic thermoelectric materials [94,95]. And making it comparable to advanced flexible inorganic thermoelectric materials. Moreover, even after crosslinking treatment, c-TEE-2 maintains a *ZT* value of 0.23 [94] and exhibits a high power factor of 363 $\mu W\ m^{-1}\ K^{-2}$. Notably, these materials exhibit a unique strain-insensitive characteristic. Even under 150% tensile strain, their electrical conductivity and power factor remain at relatively high levels. In contrast, the electrical conductivity of conventional conjugated polymers typically decreases by more than 25-fold when subjected to 100% strain. This outstanding stability enables electronic skin to efficiently convert temperature differences between the body surface and the surrounding environment into electrical energy, even during continuous human motion. For example, when the skin and the ambient environment serve as the hot and cold sides, respectively ($\Delta T = 4$ K), a TEE-based thermoelectric device can generate an output voltage of 1.30 mV, which is sufficient to power low-power biosensors. Moreover, an out-of-plane device architecture conformally attached to the wrist can produce an output voltage of 2.37 mV while maintaining stable performance under dynamic bending conditions. From the DEOS strategy for eliminating signal crosstalk, to three-dimensional micro-lattice architectures that buffer external mechanical stresses, and further to n-type thermoelectric elastomers that unify mechanical compliance and thermoelectric performance, the evolution of flexible thermoelectric materials has fundamentally closed the technological loop between self-sustained energy supply and microenvironmental sensing in wearable devices. These advances have paved the way for the realization of truly self-powered intelligent electronic skin systems.

4.2.2. *Applications of ionic thermoelectric materials in electronic skin*

Compared with body-temperature monitoring, which mainly focuses on whether temperature can be accurately read out, electronic skin must also achieve large-area conformal contact, spatial mapping of local thermal fields, and stable adhesion during repeated deformation. Therefore, the role of ionic thermoelectric materials in electronic skin is not limited to increasing the thermovoltage generated by a temperature difference. They can also form soft, arrayed sensing layers that conform to complex surfaces and move synchronously with the skin. Sun et al. [76] introduced GO into a PAM/BMIM ionic gel, and the interactions between GO and the polymer network improved the mechanical integrity and ionic thermoelectric stability of the gel. The resulting ionic gel

film exhibited a Seebeck coefficient of −76.7 mV K^{-1}, a power factor of 753.0 μW m^{-1} K^{-2} at 383 K, and a ZT of 0.19. It also showed a tensile strength of 219.7 kPa and an elongation at break of 389%. The film retained its self-adhesion after being bent through 180° and maintained a relatively high power factor after 7 days of attachment. A flexible device comprising nine thermoelectric legs, with dimensions of 25 × 25 mm^2, achieved a maximum power density of 1.32 mW cm^{-2} at a temperature difference of 20 K. These results indicate that continuous, flexible ionic thermoelectric layers can reduce interfacial mismatch between rigid thermoelectric legs and the skin, providing a suitable materials basis for conformal thermal sensing in electronic skin.

When electronic skin is required to simultaneously identify temperature and mechanical deformation, ionic thermoelectric gels can also be combined with ionic resistive sensing mechanisms to enable multimodal signal acquisition. Ding et al. [96] developed an n-type thermoelectric ionic gel with a double-network structure that can simultaneously acquire temperature and strain signals. The gel can monitor joint movements of the fingers, wrists, and elbows, recognize subtle facial expressions such as frowning, and further acquire electrocardiogram and electromyography signals (ECG and EMG). Its self-adhesive property enables stable attachment to the skin, while the material maintains stable sensing performance over an ambient temperature range of −10 °C to 45 °C [96]. This system illustrates that ionic thermoelectric materials can provide temperature responses while also enabling the simultaneous acquisition of strain and physiological signals through the ion-conducting network.

For applications requiring self-healing, extreme deformation, and skin adhesion, Wang et al. [69] developed an A1D1-CD20 supramolecular ionic hydrogel. Host–guest interactions, hydrogen bonding, and electrostatic interactions jointly maintain its network structure, giving the hydrogel an elongation at break of 2173% and a tensile strength of approximately 340 kPa, together with self-healing and broad-range adhesion. With Au electrodes, its intrinsic p-type ionic Seebeck coefficient is 2.95 mV K^{-1}. An ionic thermoelectric capacitor comprising five units produces a modular response of approximately 14.3 mV K^{-1} at a temperature difference of 1 K. The different sensing signals in this material should be distinguished according to their origins: strain signals arise from resistance changes in the ion-conducting network, whereas temperature signals originate from the ionic thermoelectric response. Although the two signals can coexist in the same material, ordinary ionic conductivity or strain-sensing results should not be directly regarded as evidence of ionic thermoelectric performance [69].

Overall, electronic and ionic thermoelectric materials serve distinct functional roles in electronic skin. Electronic systems benefit from relatively mature micro- and nanofabrication methods and stable electrical signal output, making them suitable for multimodal signal decoupling and rapid response. Ionic systems, in contrast, offer high stretchability and thermovoltage, making them promising for reproducing the soft feel of skin and detecting small temperature differences. Their rational integration may enable a new generation of electronic skin systems with high sensitivity, flexibility, and functional integration. Beyond thermoelectric electronic skin, multifunctional fibers integrating strain sensing and supercapacitor functions have also been reported, reflecting the broader trend toward sensing-storage integration; however, their transduction mechanisms differ from those of thermoelectric sensing. Beyond body-temperature and tactile sensing, the detection of biochemical biomarkers in sweat has become another important direction in wearable health monitoring. Unlike temperature and strain, which are physical signals, biochemical signals involve changes in ion concentration and enzyme reaction kinetics. Therefore, they impose new requirements on the chemical selectivity and interfacial compatibility of thermoelectric materials, as well as their synergistic integration with recognition units.

4.3. Wearable sweat biochemical monitoring

4.3.1. Electronic thermoelectric systems for sweat biochemical monitoring

Sweat contains a wide range of biochemical biomarkers, including glucose, lactate, electrolytes (Na^+ and K^+), and metabolic products, whose concentration variations are closely correlated with human metabolic status, exercise load, and disease risks. Unlike physical signals such as body temperature and tactile stimuli, biochemical signal detection involves changes in ionic concentrations and enzymatic reaction kinetics, placing higher demands on the chemical selectivity and interfacial compatibility of sensing materials. The unique value of flexible thermoelectric sensors in this context lies in the intrinsic dual sensitivity of thermoelectric materials to temperature gradients and ionic environments, providing a physical basis for integrated biochemical detection with combined energy harvesting and sensing capabilities.

For electronic thermoelectric materials, PEDOT:PSS based organic electrochemical transistors can convert enzymatic electron transfer processes associated with glucose or lactate into current variations, but they generally require external power sources. Therefore, integrating these systems with body heat driven thermoelectric power generation modules represents a feasible strategy for realizing self-powered sweat detection. Peringeth et al. [77] constructed a flexible Bi_2Te_3/Ecoflex thermoelectric generator that could provide approximately 170 μW at a temperature difference of ΔT = 10 °C. After voltage boosting and energy storage, the device was able to power iontophoresis, Bluetooth communication, and sweat analysis. Na^+, K^+, Ca^{2+}, pH, and glucose were respectively detected through electrochemical modules based on ion selective membranes and enzyme modified electrodes, forming a system level approach integrating “thermoelectric power supply, microfluidic sampling, and electrochemical biochemical recognition”. It should be emphasized that the biochemical selectivity originates from the recognition modules rather than from the Bi_2Te_3 thermoelectric material itself.

Subsequently, among ionic thermoelectric materials, thermogalvanic systems have emerged as promising candidates for sweat biochemical detection due to their intrinsic sensitivity to ionic concentrations. In thermogalvanic cells, the electrode potential of redox couples is simultaneously regulated by temperature and ion concentration. When target analytes in sweat participate in enzymatic reactions, the resulting local heat variations and changes in ionic strength can both be detected through variations in the thermogalvanic potential [59]. However, the selectivity toward specific target molecules still relies on recognition components such as enzymes, electrodes, or ion selective membranes. Therefore, specific metabolic recognition cannot be directly attributed solely to the thermogalvanic potential.

4.3.2. Ionic thermoelectric for sweat biochemical monitoring

Furthermore, Tian et al. [78] developed a physically crosslinked double network thermoelectric hydrogel for real time sweat monitoring. The hydrogel exhibited a thermovoltage of approximately 2.04 mV K^{-1}, rapid self-healing capability within 10 min, and an electrical conductivity of 2.56 S m^{-1}. The wristband based device generated electrical signals corresponding to variations in sweat Na^+, K^+, and Ca^{2+} concentrations [78]. However, these ionic thermoelectric and thermogalvanic systems are sensitive to ionic environments and redox processes. Therefore, the selective detection of specific target analytes still requires additional recognition components, such as ion selective membranes, enzymes, or electrode interfaces. Specific identification of individual metabolites cannot be claimed solely based on thermoelectric voltage output.

Overall, in sweat biochemical detection applications, electronic and ionic thermoelectric materials exhibit more distinct functional roles. Ionic thermoelectric systems, benefiting from their intrinsic sensitivity to ionic concentrations and redox reactions, can directly participate in the conversion of biochemical signals. In contrast, electronic thermoelectric systems, with their rapid response and stable electrical signal

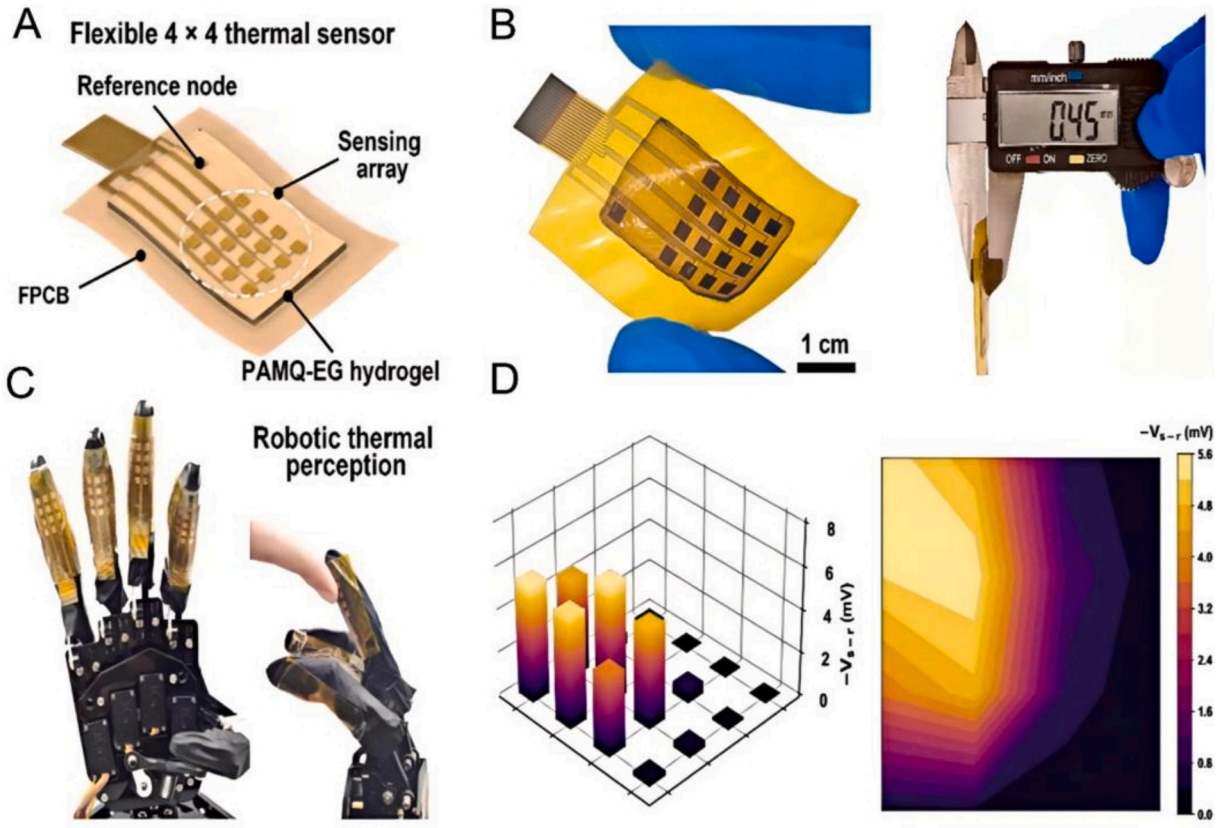


Fig. 7. Organic thermogalvanic hydrogel-based thermal sensor array for robotic thermal tactile sensing and spatial temperature mapping. (A) Schematic illustration of the 16-node thermal sensor array on a flexible printed circuit board, with a shared reference node. (B) Photograph of the flexible sensor array, showing a thickness of approximately 0.45 mm. (C) Photographs of a robotic hand integrated with the thermal sensor arrays. (D) Sensing node responses and the corresponding smoothed voltage map, revealing the thermal contour of a human finger. (A-D) Reproduced with permission from Ref. [80]. Copyright 2025, Elsevier.

output, serve complementary roles in temperature compensation, signal amplification, and system integration. The synergistic integration of these two types of materials may enable wearable biochemical sensing platforms that operate without external power sources and simultaneously monitor multiple sweat biomarkers. Beyond sweat biochemical detection, the application of flexible thermoelectric sensors in robotic bionic perception represents another emerging research direction in recent years. Unlike human health monitoring, robotic applications impose different requirements on sensors, including response speed, spatial resolution, and interference resistance.

4.4. Biomimetic thermal sensing in robots

Biomimetic thermal sensing in robots involves more than measuring temperature. It also includes locating heat sources, reconstructing temperature fields, identifying contact materials, and triggering protective responses under hazardous thermal stimuli. Flexible thermoelectric sensors can directly convert temperature differences into electrical signals and conform to curved surfaces through thin-film, island–bridge, fiber, and hydrogel structures. They are therefore well suited for integration onto robotic hands, soft robots, and bioinspired electronic skin. More broadly, bioinspired sensing provides the perceptual basis for human-like robotic behavior and safe human–robot interaction, while flexible and large-area tactile skins are increasingly being developed to improve compliant interaction and environmental perception in robotic systems [97].

Based on the mechanisms responsible for thermoelectric signal generation, this section discusses the roles of electronic and ionic thermoelectric systems in robotic thermal sensing. Following the functional progression from thermal detection to thermal tactile sensing and thermal nociception, it further analyzes how flexible thermoelectric sensors can evolve from simple temperature measurement into biomimetic sensing systems capable of protective responses.

4.4.1. Electronic thermoelectric systems: Noncontact thermal detection and array-based temperature mapping

Electronic thermoelectric materials generate signals through the transport of charge carriers such as electrons and holes. They generally offer fast response, stable output, and straightforward array integration. Accordingly, these materials have been used primarily for noncontact heat-source detection and temperature mapping in robotic systems. Guo et al. [79] developed a flexible infrared photothermoelectric detector consisting of Te/CuTe multilayer films and a polyimide substrate. The device uses the photothermoelectric effect for noncontact thermal sensing, resolving temperature changes as small as 0.05 °C and providing a response time of approximately 154 ms. It maintains stable photovoltage output over a temperature range of −50 to 110 °C. The researchers further constructed a 4 × 4 thermopile array for spatial imaging of infrared radiation. When the detector was integrated at the front end of a soft robotic gripper, the system could determine whether a heat source posed a potential hazard before physical contact by analyzing its temperature and the slope of the response voltage. It could then control whether to continue or stop the grasping action, thereby providing a thermal early-warning function for safe interaction.

When a robot needs to obtain the temperature distribution of a contact area or a large surface, the sensor must provide not only rapid heat-source detection but also scalable spatial organization and sufficient mechanical compliance. Kang et al. [98] constructed a 4 × 4 island–bridge temperature-sensitive electronic skin using Bi—Te microthermoelectric generators, a PDMS substrate, and serpentine

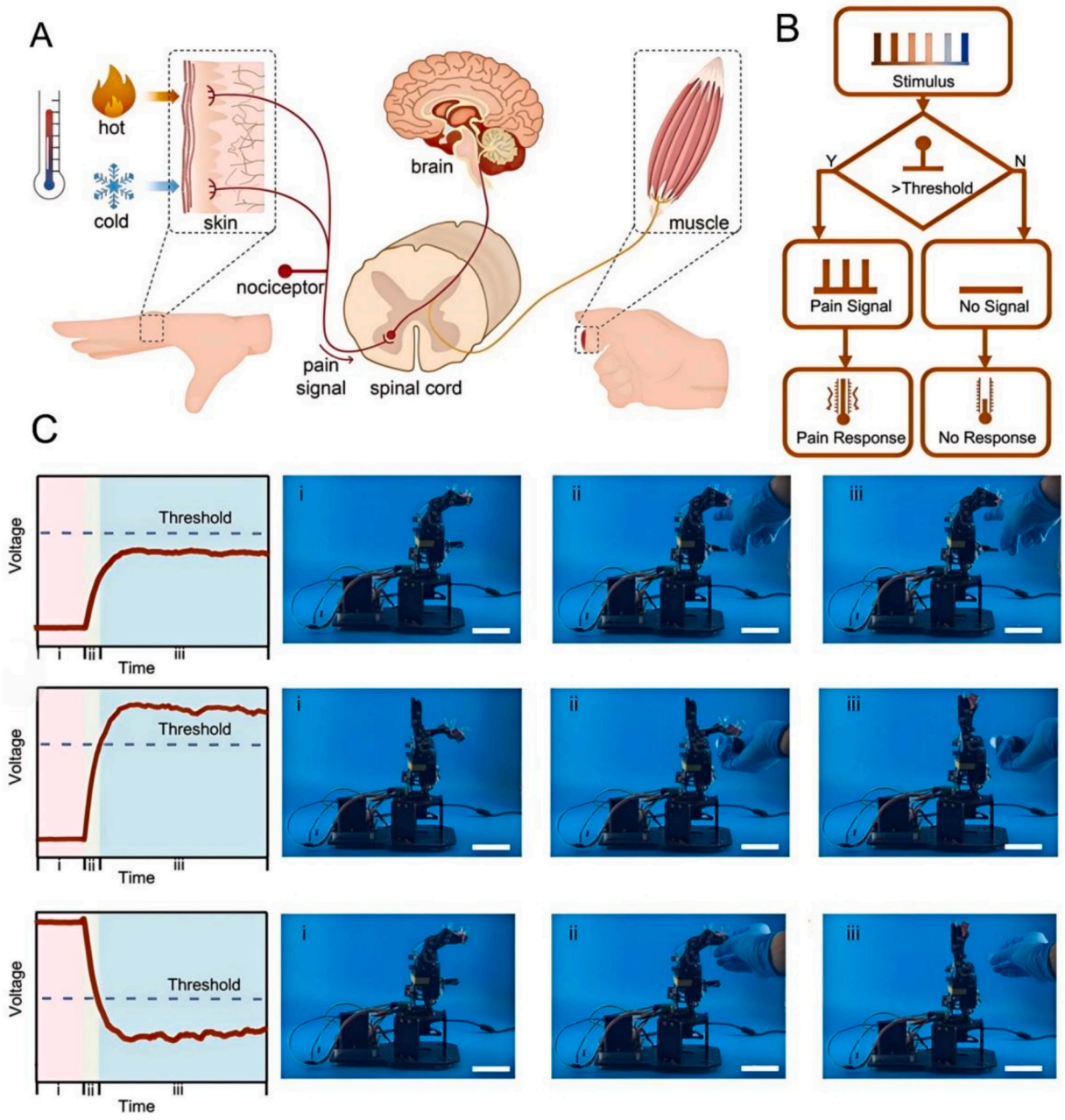


Fig. 8. Thermoelectric artificial nociceptor for robotic thermal pain perception. (A) Schematic illustration of the biological nociceptive system, in which thermal stimuli are transduced into pain signals. (B) Threshold-based functional flow diagram of the artificial thermoreceptor. (C) Protective responses of the robotic arm upon contact with a human finger, hot water, and an ice block. (A-C) Reproduced with permission from Ref. [81]. Copyright 2025, Springer Nature.

interconnects. The device maintained a stable temperature response under 30% tensile strain, with a sensitivity of 729 μV K^{-1} and a response time of 0.157 s. When the robotic fingers contacted a human finger, cold water, or hot water, the array spatially mapped local temperature variations. These observations indicate that the primary role of the island–bridge structure is to mitigate the deformation mismatch between rigid thermoelectric units and flexible substrates, thereby extending electronic thermoelectric devices from point temperature measurements to large-area, multi-unit temperature-field sensing.

For applications involving thermal safety and thermal nociception, the temporal stability and spatial uniformity of the temperature signal are also critical. Only when device output exhibits low temporal and spatial fluctuations can subsequent temperature grading, threshold determination, and protective control be implemented reliably. Recent work combined photoinduced n-type doping with junction-free p–n integrated patterning to construct a high-reliability thermoreceptor [81]. The resulting devices exhibited temporal variation below 1% and spatial variation of 4.54%, providing a stable thermoelectric signal basis for subsequent thermal-stimulus discrimination and protective control. When integrated into a robotic arm, the thermoreceptors enabled the system to distinguish harmless and harmful thermal contacts and initiate corresponding protective actions.

4.4.2. Ionic thermoelectric systems: Flexible thermal tactile sensing and contact-material identification

In contrast to electronic thermoelectric systems, ionic thermoelectric materials generate voltage mainly through ion migration driven by a temperature gradient and electrode redox reactions in thermogalvanic cells. Hydrogels, ionogels, and thermogalvanic-cell materials typically exhibit high thermovoltages and good mechanical compliance, making

them suitable for covering robotic surfaces, joints, and other regions subject to large deformation. Shen et al. [80] developed an organic thermogalvanic hydrogel thermal-sensor array based on a benzoquinone/hydroquinone redox couple. The system had an ionic Seebeck coefficient of 1.57 mV K^{-1} and a response time of approximately 0.4 s. Four sensing nodes and a central heating coil were integrated onto a flexible printed circuit board. Through pulsed heating, sequential acquisition of temperature signals, and an LSTM neural network, the system identified seven different materials with a classification accuracy of 98.8%. The researchers also constructed a high-density array containing 16 sensing nodes, which spatially imaged letter-shaped heat sources over an area of 1.5 cm × 1.5 cm. After integration onto a robotic gripper, the array identified the thermal contour of a human finger during contact, demonstrating that ionic thermoelectric systems can contribute not only to temperature measurement but also to contact-based thermal tactile sensing. The device structure and thermal sensing performance of this hydrogel-based array are summarized in Fig. 7. As shown in Fig. 7A, the 16 sensing nodes, together with a shared reference node, are integrated on a flexible printed circuit board. The overall thickness is approximately 0.45 mm, enabling conformal contact with curved surfaces (Fig. 7B). When mounted on a robotic hand (Fig. 7C), the array resolves the thermal contour of a human finger during contact, as shown by the voltage map in Fig. 7D.

Material identification requires more than simply increasing the thermovoltage. It also requires distinguishing differences in heat diffusion and interfacial heat transfer among materials. The sensor must therefore generate a sufficiently strong electrical signal while preserving temporal features associated with the heat-transfer process. Cai et al. [99]constructed a biomimetic ionic thermoreceptor with an anisotropic thermal-response structure. Through spatially differentiated sensing units, the device encoded thermal signals into response patterns with distinct temporal features, enabling simultaneous extraction of thermal contact signatures and absolute temperature information. The system achieved a material-identification accuracy of 98.9% and a temperature resolution of 0.81 mK, together with good mechanical stability, signal stability, and environmental adaptability [99]. This study shows that the advantage of ionic thermoelectric systems lies not only in their high thermovoltage. More importantly, ion migration and heat diffusion can generate thermal tactile signals with a temporal dimension. For robots, these signals can be used to identify contact materials, detect temperature changes, and monitor potential thermal hazards. The soft ionic-conductive network also facilitates continuous conformal contact between the sensor and complex surfaces.

Thus, ionic thermoelectric materials are particularly suitable for flexible, stretchable, and skin-conformal thermal sensing, especially distributed temperature detection and contact-material identification on robotic surfaces. Their output, however, can be affected by water content, ion concentration, ambient humidity, and encapsulation conditions. Long-term stability in practical robotic systems therefore still requires structural encapsulation, environmental calibration, and signal decoupling.

4.4.3. *From temperature readout to thermal nociception*

Temperature measurement and thermal nociception are not equivalent. The former focuses mainly on accurately reading temperature values or temperature distributions, whereas the latter must also identify harmful thermal stimuli, establish stimulus thresholds, and trigger protective responses. A thermal nociception system therefore depends not only on the temperature-conversion capability of thermoelectric materials but also on stable threshold responses, low signal fluctuations, and coordinated operation with control units.

Recent work combined photoinduced n-type doping with junction-free p–n integrated patterning to construct a highly reliable electronic thermoelectric thermoreceptor [81]. The device exhibited temporal variation below 1%, spatial variation of 4.54%, and a voltage–temperature linearity of ($R^2 = 0.996$), providing a stable signal basis for subsequent temperature grading and threshold determination. The researchers further integrated the device into a robotic arm, enabling the system to distinguish thermal stimuli of different intensities. When the arm contacted hot water at approximately 363 K or an ice block at approximately 273 K, it produced a protective response, whereas a human finger at approximately 309 K did not trigger an obvious pain response. Based on stimulus temperature, the system classified thermal stimuli into four levels—painless, mild, moderate, and severe—with reported response times of approximately 4.3, 2.1, and 1.1 s across the graded stimuli. The classification accuracy exceeded 98.6% [81].To further illustrate how this thermoelectric nociceptor mimics biological pain perception and initiates protective actions, Fig. 8 summarizes its working principle and robotic demonstrations. Fig. 8A depicts the biological nociceptive pathway, in which thermal stimuli are converted by nociceptors into pain signals. Fig. 8B presents the threshold-based functional flow of the artificial thermoreceptor, showing that only stimuli exceeding a defined threshold generate a pain signal and a subsequent protective response. The robotic demonstrations in Fig. 8C confirm this behavior: a human finger (~309 K) does not trigger a response, whereas hot water (~363 K) causes the finger to lift rapidly, and an ice block (~273 K) causes the palm to open. These results demonstrate that the artificial nociceptor reproduces the threshold-triggered protective behavior of biological nociceptors.

These results demonstrate that electronic thermoelectric materials can provide fast, stable, and highly linear temperature inputs for robotic thermal nociception. It should be recognized, however, that thresholds, stimulus grading, and protective actions are not generated automatically by the Seebeck effect alone. They require coordinated operation among the thermoelectric sensor, signal-processing circuitry, and motion-control unit. In terms of application roles, ionic thermoelectric materials are currently better suited to flexible thermal tactile sensing and contact-material identification. For example, the aforementioned anisotropic ionic thermoreceptor can distinguish different materials using the temporal features of thermal signals and achieve high-resolution temperature monitoring [99]. Electronic thermoelectric devices, by comparison, have been further used for thermal-hazard grading and the triggering of protective actions. In robotic systems, the two types of materials correspond to separate functional stages, such as flexible contact sensing and rapid thermal-risk assessment, and represent complementary functions rather than a simple performance substitution.

It is acknowledged that electronic and ionic thermoelectric materials serve distinct functions in biomimetic thermal sensing for robots. Electronic thermoelectric systems are mainly used for rapid heat-source detection, temperature-field imaging, and thermal-hazard threshold triggering. Ionic thermoelectric systems are better suited to flexible conformal contact, contact-based thermal tactile sensing, and material identification. The former emphasizes stable, rapid, and array-based temperature-signal output, whereas the latter emphasizes compliant interfaces, ionic thermoelectric responses, and the encoding of temporal information during contact. In the future, the two types of systems can be integrated selectively according to the location and sensing task within a robot. Electronic thermoelectric devices can perform rapid thermal-safety assessment, while ionic thermoelectric devices can provide flexible contact sensing, thereby forming biomimetic thermal-sensing systems with clearly differentiated functions. Beyond biomimetic thermal sensing in robots, flexible thermoelectric sensors are also being applied to fire early warning, underwater detection, and other environmental-monitoring scenarios. These applications impose different requirements on temperature tolerance, waterproofing, long-term stability, and adaptability to complex environments.

5. Applications of flexible thermoelectric sensors in environmental monitoring

Beyond biosensing, flexible thermoelectric sensors also show considerable potential for environmental monitoring. Compared with

Table 2-1
Performance metrics of representative flexible thermoelectric sensors in environmental monitoring.

Material system	Key metrics	Application	Ref.
MXene/AgNW/ aramid textile	Operating temperature = 100–400 °C; response time = 1.6 s	Fire warning (electronic)	[101]
rGO/PVA/glycerol organohydrogel	S = 1.67 MV K^{-1}; response time = 0.34 s	Fire warning (ionic)	[102]
TEPUF	Waterproof ; temperature-strain decoupling; compression cycles = 20,000	Underwater monitoring (electronic)	[19]
TEPUF + SVM + logic circuit	Graded warning = SAFE/ WARNING/SOS	Intelligent system (electronic)	[19]

Note: "S" denotes Seebeck coefficient. For ionic systems, S is reported as the ionic Seebeck coefficient in mV K^{-1}. Values are intended for qualitative comparison.

human health monitoring, environmental applications impose stricter requirements on temperature tolerance, long-term stability, and environmental adaptability. Fire early warning emphasizes rapid response at high temperatures, whereas underwater monitoring requires stable output under highly humid or immersed conditions. Large-scale environmental sensing also relies on the coordinated operation of distributed sensor networks. Accordingly, this section focuses on fire early warning, multimodal underwater monitoring, and intelligent environmental sensing systems. In addition to direct thermoelectric sensing, flexible thermoelectric generators can provide power for other environmental sensors. For example, an organic thermoelectric generator integrated with an organic transistor gas sensor enabled self-powered ammonia detection without an external power supply [100], Table 2-1 summarizes representative flexible thermoelectric sensors for these three application areas, together with their material systems and key performance metrics, and further compares the roles of electronic and ionic thermoelectric materials under different environmental conditions.

5.1. Fire monitoring

In specialized environmental-monitoring scenarios, early fire warning is of critical importance for public safety. Conventional fire alarm systems, such as smoke detectors and heat detectors, rely heavily on smoke concentration or predefined temperature thresholds, often resulting in delayed responses and a dependence on external power supplies. In contrast, flexible thermoelectric sensors based on the Seebeck effect can directly utilize the large temperature gradients generated during a fire to drive the directional migration of charge carriers, thereby converting thermal energy into electrical signals. This self-powered capability makes them an ideal platform for achieving real-time, highly sensitive fire detection and monitoring [103]. In fire-monitoring applications, the central challenge lies in enabling sensors to maintain efficient thermoelectric conversion and structural stability while withstanding severe thermal shocks at elevated temperatures. As shown in Fig. 9, Ding et al. systematically summarized the charge-carrier transport mechanisms and performance-enhancement strategies of various thermoelectric materials for fire-warning applications. In order to comprehensively elucidate the response mechanisms of thermoelectric materials in fire warning applications, the research team conducted a systematic analysis of both inorganic and organic material systems. For

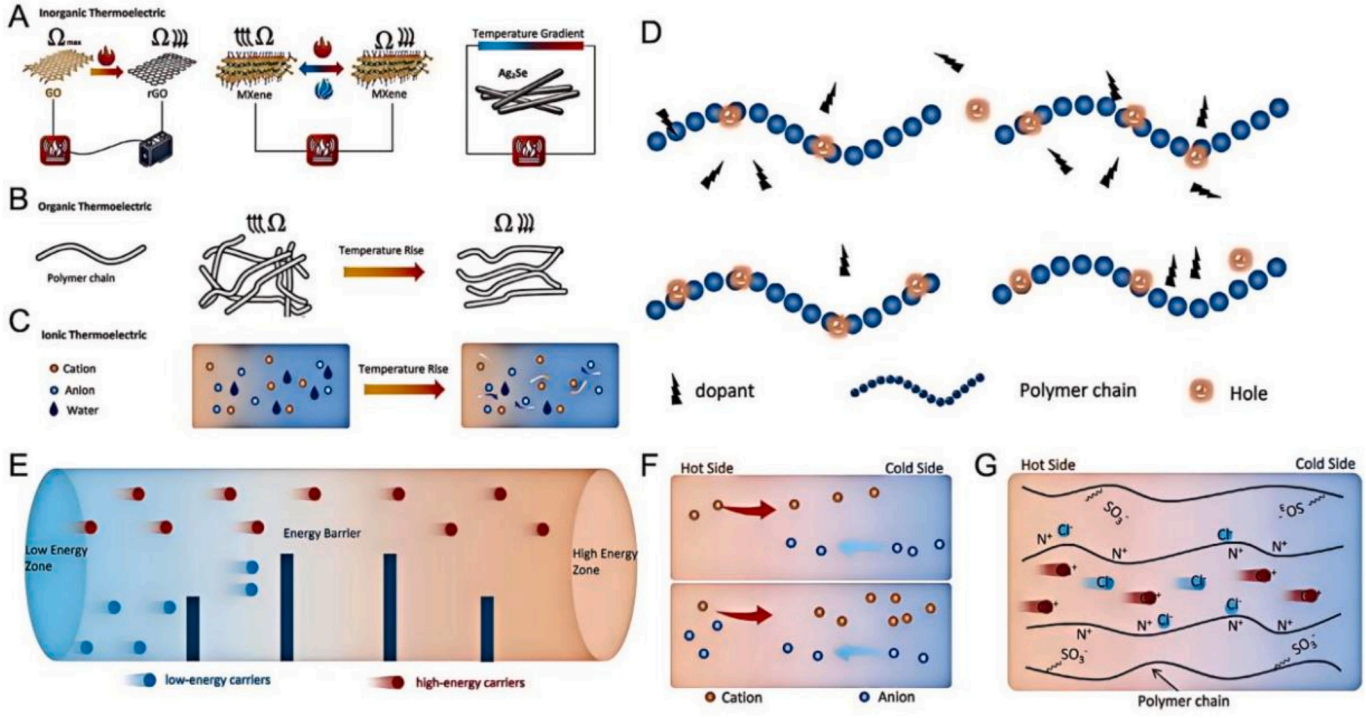


Fig. 9. Materials and Mechanisms for Thermoelectric Fire Warning. (A) Charge-carrier migration mechanism in inorganic thermoelectric materials under a temperature gradient. (B) Evolution of charge-carrier transport behavior in organic thermoelectric materials with increasing temperature. (C) Asymmetric ion migration in ionic thermoelectric materials under a temperature gradient. (A-C) Reproduced with permission from Ref. [109]. Under the terms of the Creative Commons Attribution–NonCommercial License (CC BY-NC 4.0). (D) Dopant-regulated charge-carrier transport mechanism in polymer chains. Reproduced with permission from Ref. [104]. Copyright 2023, Springer Nature B.V. (E) Interfacial-barrier-mediated energy-filtering effect, in which low-energy charge carriers are selectively scattered to enhance the Seebeck coefficient. Reproduced with permission from Ref. [109]. Under the terms of the Creative Commons Attribution–NonCommercial License (CC BY-NC 4.0). (F) Formation of the ionic thermoelectric potential driven by a temperature gradient. Reproduced with permission from Ref. [109]. Under the terms of the Creative Commons Attribution–NonCommercial License (CC BY-NC 4.0). (G) Synergistic enhancement mechanism of thermoelectric performance through ion migration and interfacial coupling within polymer networks. Reproduced with permission from Ref. [108]. Copyright 2022, The Royal Society of Chemistry.

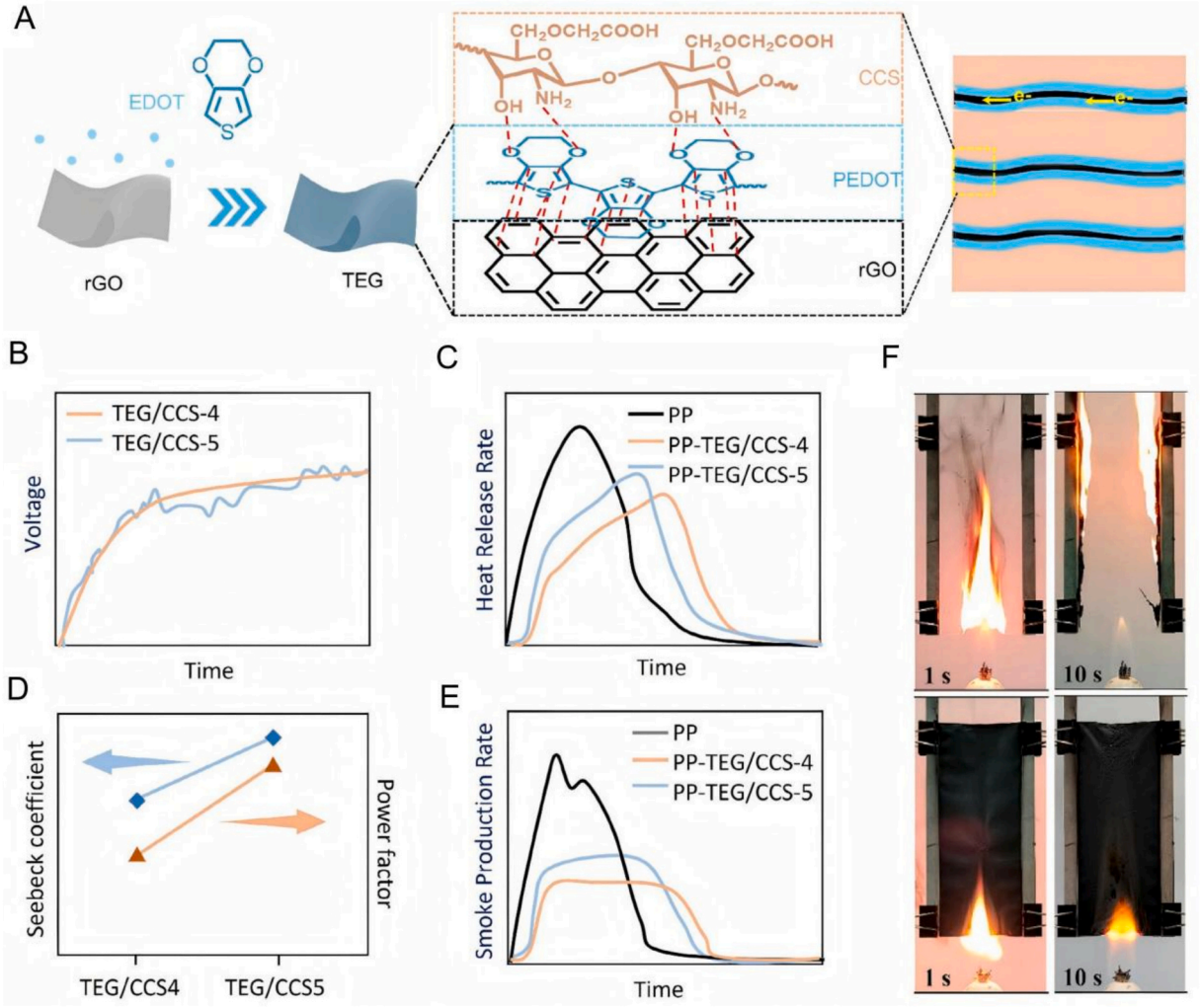


Fig. 10. Layered PEDOT-Functionalized Reduced Graphene Oxide (rGO) Heterostructure and Its Thermoelectric Fire-Warning Performance. (A) Schematic illustration of the in situ polymerization of PEDOT to form thermoelectric graphene (TEG) and the construction of the TEG/CCS layered conductive network. (B) Time-dependent thermoelectric output voltages of different TEG/CCS systems. (C) Heat release rates of different materials during combustion. (D) Effects of the layered heterostructure on the Seebeck coefficient and power factor. (E) Smoke release rates of different material systems during combustion. (A-E) Reproduced with permission from Ref. [109]. Copyright 2021 the terms of the Creative Commons Attribution–NonCommercial License (CC BY-NC 4.0). (F).Comparison of the combustion behaviors of different composites, demonstrating the superior flame-retardant performance of the PEDOT/rGO/CCS system. Reproduced with permission from Ref. [110]. Copyright 2024 Elsevier B.V.

inorganic thermoelectric materials, when a fire induces a sharp local temperature rise, a significant temperature gradient develops within materials such as graphene oxide (GO), MXenes, and Ag_2Se. This gradient drives electrons or holes to migrate from the hot side to the cold side, rapidly generating a thermoelectric voltage signal, which provides a critical foundation for self-powered fire warning systems (Fig. 9A). In contrast, the response mechanism of organic thermoelectric materials during heating primarily manifests as the rearrangement of molecular chains and the evolution of charge-carrier transport behavior: the increase in temperature promotes orderly alignment of polymer chains and significantly enhances charge transport efficiency, enabling these materials to exhibit excellent response performance in flexible and wearable fire monitoring systems (Fig. 9B). In Fig. 9C, it reveals the operating mechanism of ionic thermoelectric materials. Under the influence of a temperature gradient, cations and anions undergo asymmetric migration, generating thermoelectric potentials that are substantially higher than those produced by conventional electronic thermoelectric materials. This feature provides a new technological pathway for ultrasensitive fire-warning systems. Beyond the intrinsic charge-carrying mechanisms of different thermoelectric materials, recent research has increasingly focused on further enhancing thermoelectric performance through strategies such as interfacial engineering, doping engineering, and ion-transport regulation. As illustrates in Fig. 9D [104], in conductive polymer systems, the incorporation of appropriate dopants can regulate the charge-carrier concentration within the polymer chains and optimize charge transport pathways throughout the conjugated network. During the doping process, interactions between the dopant ions and polymer chains promote the formation of a more continuous conductive network, facilitating charge-carrier transport while simultaneously enhancing electrical conductivity and maintaining a high thermoelectric output. Consequently, a more stable electrical signal can be generated, providing a reliable basis for subsequent fire-warning applications. Furthermore, as illustrated in Fig. 9E, researchers have proposed an energy-filtering strategy in which potential barriers are engineered at the interfaces between different materials. These interfacial barriers preferentially scatter low-energy charge carriers while allowing high-energy carriers to participate in electrical transport, thereby effectively enhancing the Seebeck coefficient while minimizing adverse effects on electrical conductivity [105,106]. Compared with conventional strategies that rely solely on

increasing the carrier concentration, energy filtering enables simultaneous optimization of the Seebeck coefficient and electrical conductivity, resulting in a higher power factor. Consequently, it has become an important design strategy for developing high-performance thermoelectric materials in recent years. In addition to regulating electronic transport, the ionic thermoelectric effect provides a new strategy for enhancing the performance of fire-warning devices. As illustrated in Fig. 9F, under a temperature gradient, cations and anions undergo asymmetric migration owing to their different thermodiffusion behaviors, resulting in spatial charge separation and the establishment of a thermoelectric potential within the system [107]. Compared with conventional electronic thermoelectric materials, this mechanism can achieve Seebeck coefficients that are orders of magnitude higher, making it particularly attractive for self-powered fire-monitoring applications operating under small temperature gradients. Fig. 9G [108] further illustrates the synergistic mechanism between ion migration and the polymer network. By incorporating ion-conducting polymers or ionic liquids into the polymer matrix, the migration rates of different ionic species can be regulated while suppressing the random diffusion of selected ions, thereby generating a more stable thermoelectric potential. Meanwhile, the polymer network provides continuous ion-transport pathways, further enhancing the stability of the thermoelectric response and enabling the device to maintain stable thermoelectric output throughout the continuous temperature rise during a fire. Overall, current research on thermoelectric materials for fire-warning applications has primarily focused on three complementary strategies: carrier transport regulation, interfacial barrier engineering, and ionic thermoelectric enhancement. These approaches are respectively aimed at improving electrical conductivity, optimizing the Seebeck coefficient, and enhancing thermoelectric potential output. Despite targeting different aspects of thermoelectric performance, they all share the common objective of enabling a rapid and reliable response during the early stages of a fire.

It is reported that doping engineering, energy filtering, and the ionic thermoelectric effect enhance thermoelectric conversion performance through three distinct mechanisms: carrier-concentration regulation, interfacial transport optimization, and enhanced ion transport. Collectively, these strategies provide the theoretical foundation for achieving the rapid response and stable electrical output required for flexible thermoelectric materials in fire-warning applications. However, the strategies described above primarily enhance thermoelectric performance by regulating charge-carrier transport mechanisms. In practical applications, flexible fire-warning devices must simultaneously achieve rapid electrical response, efficient heat-transport regulation, and excellent flame-retardant stability. Consequently, recent research has increasingly focused on optimizing the microstructure of thermoelectric materials through the construction of layered heterostructures and continuous conductive networks to further improve fire-warning performance [109].

Most practical fire-warning examples discussed above rely on electronic thermoelectric conversion. The ionic thermoelectric mechanism already introduced which provides a complementary route, but it should be discussed as a separate signal-generation mode rather than as another electronic transport strategy. From an application standpoint, electronic thermoelectric materials are suited to rapid voltage output, direct circuit integration, and operation in high-temperature warning nodes, whereas ionic thermoelectric materials can provide a large temperature-induced potential for detecting an early or relatively small temperature rise. The two modes can therefore be incorporated into the same fire-warning architecture with different responsibilities, without treating one as a replacement for the other.

To simultaneously achieve high thermoelectric conversion efficiency, mechanical robustness, and flame-retardant performance, researchers have recently proposed a conductive-network design strategy based on layered heterostructures. By constructing continuous electron-transport pathways and regulating the interfacial interactions between different components, this strategy simultaneously enhances charge-carrier transport efficiency and structural stability, providing a promising design approach for next-generation flexible thermoelectric materials for fire-warning applications. As shown in Fig. 10 A [109], 3,4-ethylenedioxythiophene (EDOT) was first polymerized in situ on the surface of reduced graphene oxide (rGO) to form PEDOT-functionalized thermoelectric graphene (TEG). Subsequently, the TEG was co-assembled with carboxymethyl chitosan (CCS) to construct a layered heterostructure. Within this architecture, PEDOT and rGO formed a continuous conductive framework, while CCS reinforced the interlayer adhesion through hydrogen bonding, establishing robust interfacial connections between the different components. As a result, the interfacial resistance to electron transport was significantly reduced, facilitating charge-carrier transport and providing a stable conductive network for efficient thermoelectric output [110].To evaluate the influence of the layered conductive network on thermoelectric response, Fig. 10B [109] presents the thermoelectric output voltages of different TEG/CCS systems. As the conductive network becomes progressively established, the devices rapidly generate stable thermoelectric outputs. Notably, the optimized TEG/CCS-5 consistently exhibits the highest output voltage, indicating that appropriate regulation of the PEDOT-to-CCS ratio effectively improves charge-carrier transport efficiency and enhances the thermoelectric response during the early stages of a fire. As shown in Fig. 10C [109], the incorporation of TEG/CCS significantly reduces the heat release rate compared with pristine polypropylene (PP). This improvement is attributed to the synergistic effect of PEDOT and rGO, which promotes the formation of a continuous carbonaceous protective layer at elevated temperatures. The resulting char layer effectively suppresses heat transfer into the bulk material and retards the thermal decomposition of the polymer matrix, thereby slowing fire propagation and significantly enhancing the flame-retardant performance of the material. Furthermore, Fig. 10D [109] compares the Seebeck coefficient and power factor of different composite systems. It can be seen that both key thermoelectric parameters are significantly improved following the construction of the layered conductive network. These results indicate that PEDOT functionalization not only enhances charge-carrier transport but also optimizes the carrier transport pathways, enabling the material to achieve a higher thermoelectric output while maintaining high electrical conductivity. Fig. 10E [109] further compares the smoke release rate of different material systems during combustion. Compared with pristine polypropylene (PP), the incorporation of TEG/CCS markedly reduces the peak smoke release rate. This result indicates that the layered carbonaceous barrier not only suppresses heat transfer but also effectively inhibits the release of combustible volatile products, thereby reducing smoke generation during combustion and providing additional time for occupant evacuation and firefighting operations. Finally, to further evaluate the fire-protection capability of the materials, Fig. 10F presents the combustion behaviors of different samples [110]. In contrast to pristine polypropylene (PP), which burns vigorously, the PEDOT/rGO/CCS composite maintains good structural integrity during combustion and forms a stable carbonaceous protective layer on the material surface. This protective char layer effectively suppresses flame propagation, thereby significantly enhancing the fire resistance of the composite.

These results demonstrate that the layered heterostructure not only enhances the thermoelectric performance of the material but also endows it with excellent flame-retardant properties, thereby simultaneously improving both fire-warning capability and fire protection. Although different studies have employed diverse strategies for constructing conductive networks, they share a common objective: to simultaneously enhance thermoelectric output and flame-retardant performance through the optimization of charge-carrier transport pathways and the strengthening of interfacial stability.

In summary, through PEDOT functionalization, the construction of layered heterostructures, and interfacial synergistic engineering, significant improvements have been achieved in the continuity of

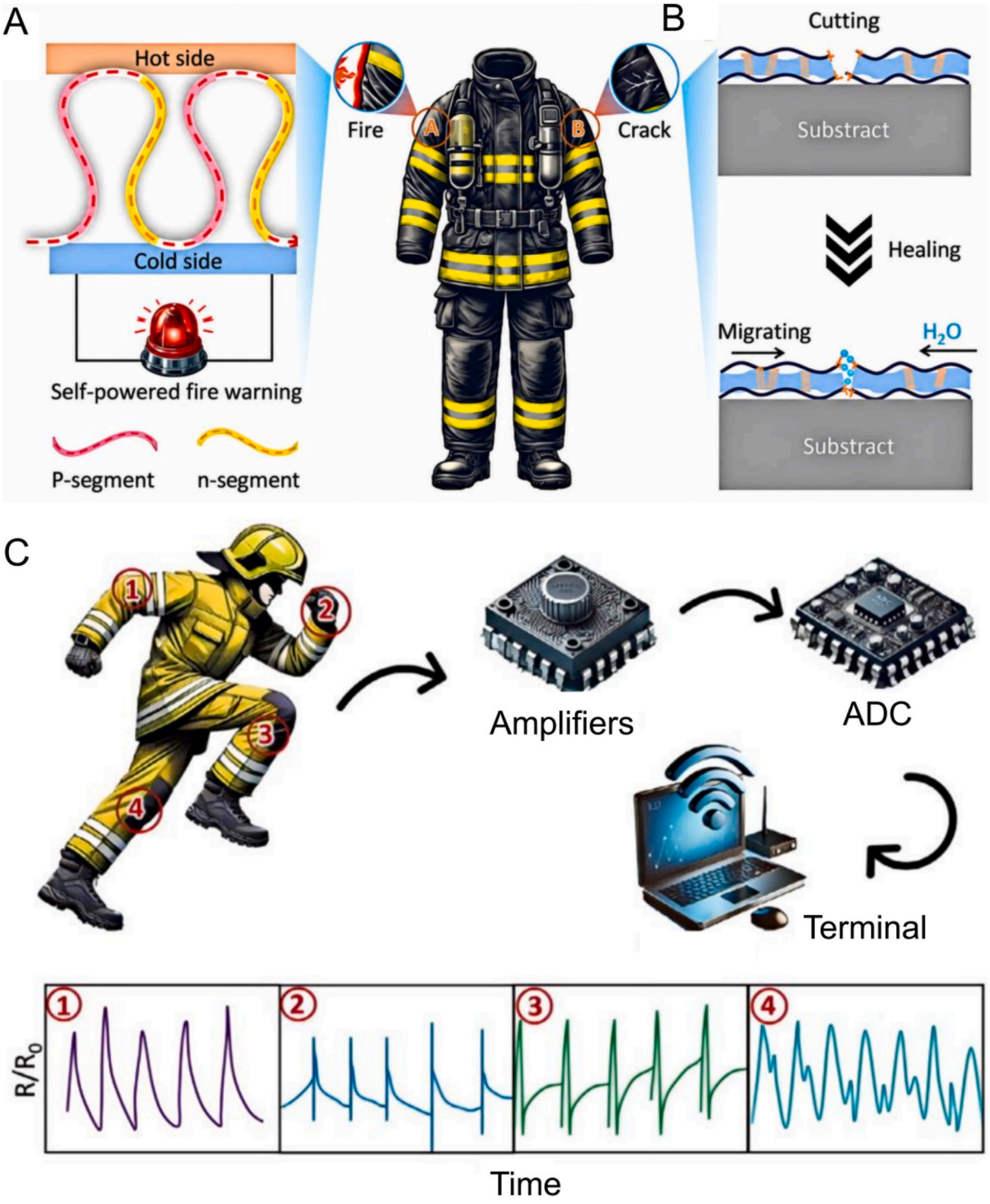


Fig. 11. Structural Design and Multifunctional Applications of Flexible Thermoelectric Fire-Warning Devices. (A) Flexible self-powered fire-warning device constructed from Ag_2Se/PI/HAP composite aerogel fibers. Reproduced with permission from Ref. [112] under the terms of the Creative Commons Attribution–NonCommercial License (CC BY-NC 4.0). (B) Self-healing mechanism of the conductive network based on dynamic chemical bonds for improving the long-term operational stability of the device. Reproduced with permission from Ref. [113]. Copyright 2022 Elsevier B.V. (C) Application of a flexible thermoelectric sensor in human motion monitoring, where motion states are identified through the combined analysis of thermoelectric output and electrical resistance signals. Reproduced with permission from Ref. [109] under the terms of the Creative Commons Attribution–NonCommercial License (CC BY-NC 4.0).

conductive networks, charge-carrier transport efficiency, and flame-retardant stability of thermoelectric materials. These advances provide a solid material foundation for high-performance fire-warning applications. However, enhanced material properties alone do not guarantee practical device performance. For fire-monitoring applications, thermoelectric materials must be further integrated into flexible device architectures and evaluated in terms of their rapid response, long-term operational stability, and mechanical reliability under complex fire conditions. Consequently, recent studies have increasingly combined high-performance thermoelectric materials with flexible substrates,

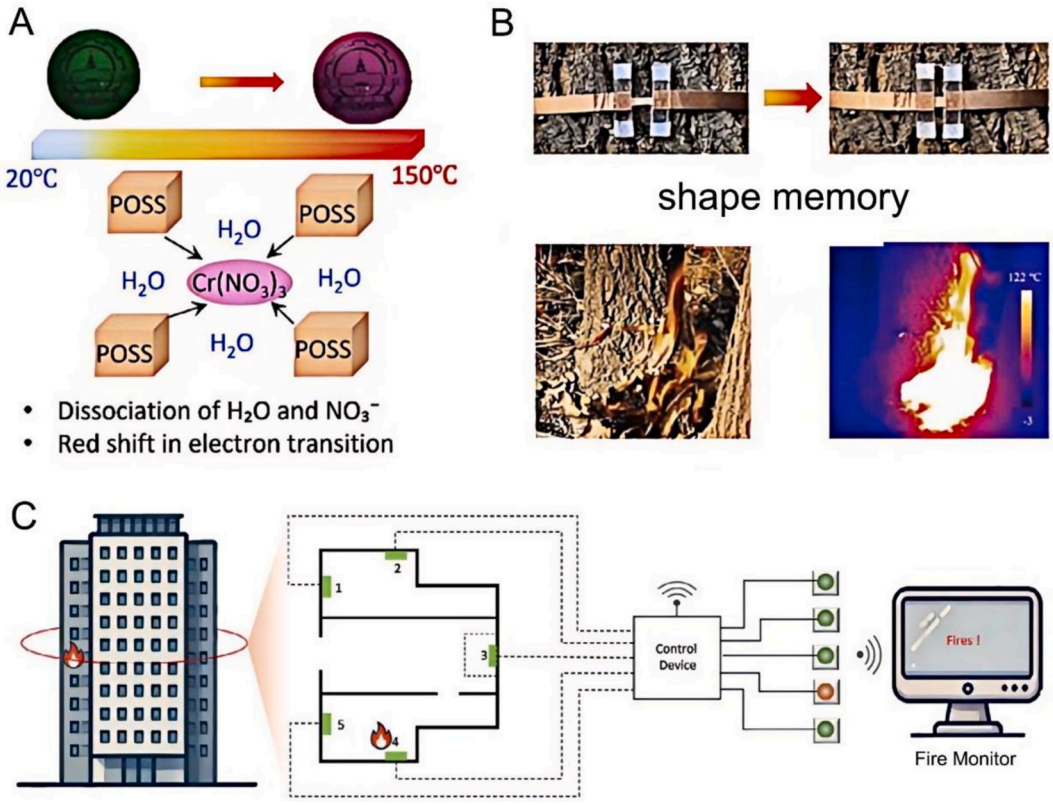


Fig. 12. Flexible Thermoelectric Materials and Intelligent Systems for Fire Monitoring and Early Warning. (A) Forest-fire early-warning material that utilizes thermochromic properties to provide a visual indication of temperature changes. Reproduced with permission from Ref. [116]. Copyright 2021 Elsevier. (B) Forest-fire early-warning material based on the shape-memory effect, capable of triggering a structural response when a predetermined temperature threshold is reached. Reproduced with permission from Ref. [117]. Copyright 2021 Elsevier B.V. (C) Residential building fire-detection and early-warning system integrating temperature monitoring, information transmission, and alarm functions. Reproduced with permission from Ref. [9]. Copyright 2023 John Wiley & Sons Ltd..

aerogel fibers, and thermoelectric junction architectures to develop fire-warning devices that simultaneously exhibit self-powered operation, mechanical flexibility, and high-temperature resistance, thereby driving the transition of flexible thermoelectric technology from materials innovation toward practical device applications.

The transition from electronic thermoelectric devices to ionic thermoelectric fire-warning layers is particularly relevant when high sensitivity must be combined with flame-retardant protection. In this case, the ion-transport mechanism and the thermal stability of the polymer network need to be considered together. Yuan et al. [107] developed a flame-retardant ionic hydrogel coating composed of gelatin/poly (acrylamide-*co*-acrylic acid), $CaCl_2$, spindle-shaped aluminum hydroxide nanosheets, and glycerol (HCA). The hydrogel combines a fracture strain of 842.5% and a tensile strength of 0.77 MPa with a Seebeck coefficient of 10.1 mV K^{-1}. During heating, the different thermodiffusion rates of Ca^{2+} and Cl^- generate a thermoelectric potential, while the gelatin/polymer network and aluminum hydroxide nanosheets contribute to adhesion and flame-retardant stability. The HCA coating was further connected to a STM32-Bluetooth alarm system, where the temperature-induced voltage triggered continuous alerts and transmitted the warning signal to a terminal. In this architecture, the ionic layer serves as a highly sensitive temperature-trigger interface, while electronic thermoelectric textiles or fibers can provide fast electronic output and direct integration with warning circuits.

Accordingly, recent research has increasingly integrated high-performance thermoelectric materials with flexible substrates, aerogel fibers, and thermoelectric junction architectures to develop fire-warning devices that simultaneously exhibit self-powered operation, mechanical flexibility, and high-temperature resistance. These advances have facilitated the translation of thermoelectric technology from materials optimization toward practical fire-monitoring applications. For example, electronic textiles integrating MXene, silver nanowires, and aramid nanofibers are capable of operating across a temperature range of 100–400 °C and can trigger a fire-warning signal through thermoelectric sensing within 1.6 s [101,111]. This exceptionally rapid response capability significantly surpasses that of conventional fire-sensing technologies. As shown in Fig. 11A [112], researchers fabricated flexible composite aerogel fibers by integrating Ag_2Se thermoelectric material, polyimide (PI), and hydroxyapatite (HAP), which were subsequently assembled into a wearable thermoelectric fire-warning device. In this architecture, PI serves as a flexible supporting framework that provides excellent mechanical compliance, HAP enhances the thermal stability and flame-retardant performance of the material, and Ag_2Se functions as the thermoelectric component responsible for thermal-to-electrical energy conversion. When a fire occurs, a temperature gradient is rapidly established across the device, enabling the thermoelectric junction to immediately generate an output voltage and activate a fire alarm without the need for an external power supply. Consequently, this device is particularly well suited for applications in firefighting garments and high-temperature protective equipment.

This design endows the fibers with excellent mechanical flexibility and signal stability at elevated temperatures, effectively overcoming the susceptibility of wearable devices to failure under extreme conditions. However, practical fire scenarios are typically characterized by prolonged high-temperature exposure and repeated mechanical deformation. Consequently, the long-term operational stability of the device is a critical factor determining the reliability of fire-warning systems [17]. As illustrated in Fig. 11B [113], researchers further introduced dynamic chemical bonds to construct a self-healing network. When the material is subjected to mechanical damage, these dynamic bonds undergo

reversible dissociation and reformation, gradually restoring the continuity of the conductive network and, consequently, the thermoelectric output. This self-healing mechanism not only prolongs the service lifetime of the device but also enhances its long-term operational stability under complex environmental conditions, thereby ensuring the reliable and continuous operation of flexible thermoelectric fire-warning devices [114].

Beyond fire-warning applications, flexible thermoelectric devices are also capable of multifunctional environmental sensing. As illustrated in Fig. 11C [109], when human joints undergo bending, stretching, or other movements, the conductive network within the device reversibly reconfigures, leading to synchronous variations in both the thermoelectric output and electrical resistance. By analyzing the characteristic response patterns associated with different motions, the system can accurately identify human movement states, thereby integrating thermoelectric sensing with motion monitoring. These results demonstrate that flexible thermoelectric devices not only enable effective fire warning but also hold considerable promise for the development of intelligent wearable sensing platforms [115] .

Through flexible device engineering, self-healing network construction, and multifunctional sensing integration, flexible thermoelectric fire-warning technology has evolved from materials research to practical device applications. These thermoelectric devices are capable not only of providing rapid fire warning at the early stages of a fire but also of maintaining long-term operational stability while simultaneously monitoring human motion, thereby offering a promising solution for fire protection, intelligent wearable systems, and environmental monitoring in complex scenarios. However, the devices discussed above are primarily designed for localized fire detection. Large-scale applications, such as forest and building fire monitoring, require the deployment of distributed thermoelectric sensing networks. Consequently, recent research has progressively expanded toward large-area environmental monitoring systems.

In large-area environmental monitoring, particularly in forest-fire surveillance where terrain is often complex and power-supply maintenance is challenging, flexible thermoelectric sensors have emerged as critical components of distributed monitoring networks. Benefiting from their self-powered capability and strong environmental adaptability, these sensors can operate autonomously over extended periods, making them highly suitable for deployment in remote and difficult-to-access environments. MXene-based intelligent sensing nodes have been demonstrated to respond rapidly to abnormal temperature fluctuations, with a response time of approximately 3.8 s. By integrating Internet of Things (IoT) communication modules, these sensors can transmit data remotely to cloud platforms in real time. This capability enables continuous environmental monitoring and improves the reliability of forest-fire surveillance, helping to mitigate the influence of complex environmental factors, such as wind speed and humidity, on fire-spread assessment and prediction. To achieve comprehensive forest-fire protection, some studies have integrated thermochromic materials into sensing systems. As shown in Fig. 12A [116], a visual forest-fire early-warning mechanism based on thermochromic materials has been developed. The material undergoes a distinct color change as the ambient temperature rises, providing an intuitive indication of fire hazards without requiring any external power supply. In Fig. 12B [117], it illustrates the application of shape-memory materials in forest-fire early-warning systems. When the temperature reaches a predetermined threshold, the material automatically recovers its preprogrammed shape, thereby triggering a mechanical alarm or an information-transmission device. Building upon this concept, Fig. 12C [9] further presents an intelligent building fire-monitoring system. Thermoelectric sensing nodes distributed throughout different areas of a building continuously collect temperature information in real time and transmit the data to a central control terminal via wireless communication, enabling fire localization and intelligent alarm activation.

The thermochromic and shape-memory examples summarized in Fig. 12 are auxiliary non-thermoelectric warning modules. They are retained to illustrate how a thermoelectric node can be combined with visual or structural alarms, rather than being classified as thermoelectric materials themselves. Fire-warning devices exploit large and rapidly developing temperature gradients, whereas underwater systems face high humidity, immersion, restricted heat exchange, and mechanical disturbance. Accordingly, the central design target changes from thermal-shock resistance and flame retardancy to waterproof flexibility, breathability, fatigue resistance, and signal decoupling. For ionic thermoelectric materials, Xiang et al. [102] developed an rGO-modified, three-dimensional spacer-fabric-reinforced PVA/glycerol organohydrogel. Anisotropic thermal conduction rapidly establishes a temperature gradient between the flame-contact region and the surrounding area, driving directional ion migration and generating a voltage signal. The material has a Seebeck coefficient of 1.67 mV K^{-1} and triggers an alarm within 0.34 s of flame contact, with its output voltage reaching 100 mV within 10 s. It retains its structural integrity after 2 min of continuous exposure to a 1000 °C flame, and takes more than 6 min to burn through. The material also combines flame retardancy with impact resistance. After integration with a Bluetooth module, the hydrogel enables wireless fire alarms and impact-event recording [102].

A gelatin-based HCA ionic hydrogel has a Seebeck coefficient of up to 10.1 mV K^{-1} and an elongation at break of 842.5%, and can produce a continuous fire-alarm signal. A Gly-GAPL multicrosslinked gelatin composite hydrogel has a Seebeck coefficient of 8.66 mV K^{-1} and triggers an alarm within 2 s of flame contact, while also offering transparency, adhesion, and flame retardancy [80,107,118]. These ionic systems use their high thermovoltage and flame-retardant, water-retaining networks to trigger alarms in response to small temperature differences. Their long-term performance, however, remains affected by water retention, ion migration, and interfacial reactions at high temperatures.

Overall, electronic and ionic thermoelectric materials serve distinct roles in fire early warning. Electronic systems benefit from mature conductive-network designs and rapid response, making them well suited to early detection of temperature anomalies and continuous signal output. Ionic systems, with their high thermovoltage and compatibility with flame-retardant designs, show promise for triggering alarms in response to small temperature differences. Combining the two could enable comprehensive warning from the incipient to the developing stages of a fire.

5.2. *Multimodal underwater environmental monitoring*

The environmental constraints of underwater monitoring make the distinction between the thermoelectric carrier and the sensing interface especially important. The following TEPUF case is an electronic thermoelectric system in which the thermoelectric coating, porous support, and piezoresistive channel perform different functions. As thermoelectric technology transitions from laboratory research to practical deployment, the stability and multifunctionality of materials in complex environments have become major focuses of current research. Particularly for flexible organic thermoelectric materials, a critical challenge that remains to be addressed is how to maintain stable performance under high-humidity or even underwater conditions, while simultaneously achieving accurate sensing of environmental signals. Although conventional encapsulation strategies can provide effective waterproof protection, they often do so at the expense of breathability and mechanical flexibility, thereby limiting their applicability in long-term wearable systems and dynamic environmental-monitoring scenarios. To address this challenge, recent research has proposed a “material-structure-algorithm” co-design strategy, leading to the development of a thermoelectric polyurethane foam (TEPUF) that combines waterproofness, high breathability, and exceptional elasticity. This approach establishes a new paradigm for the application of thermoelectric materials in underwater environmental monitoring.

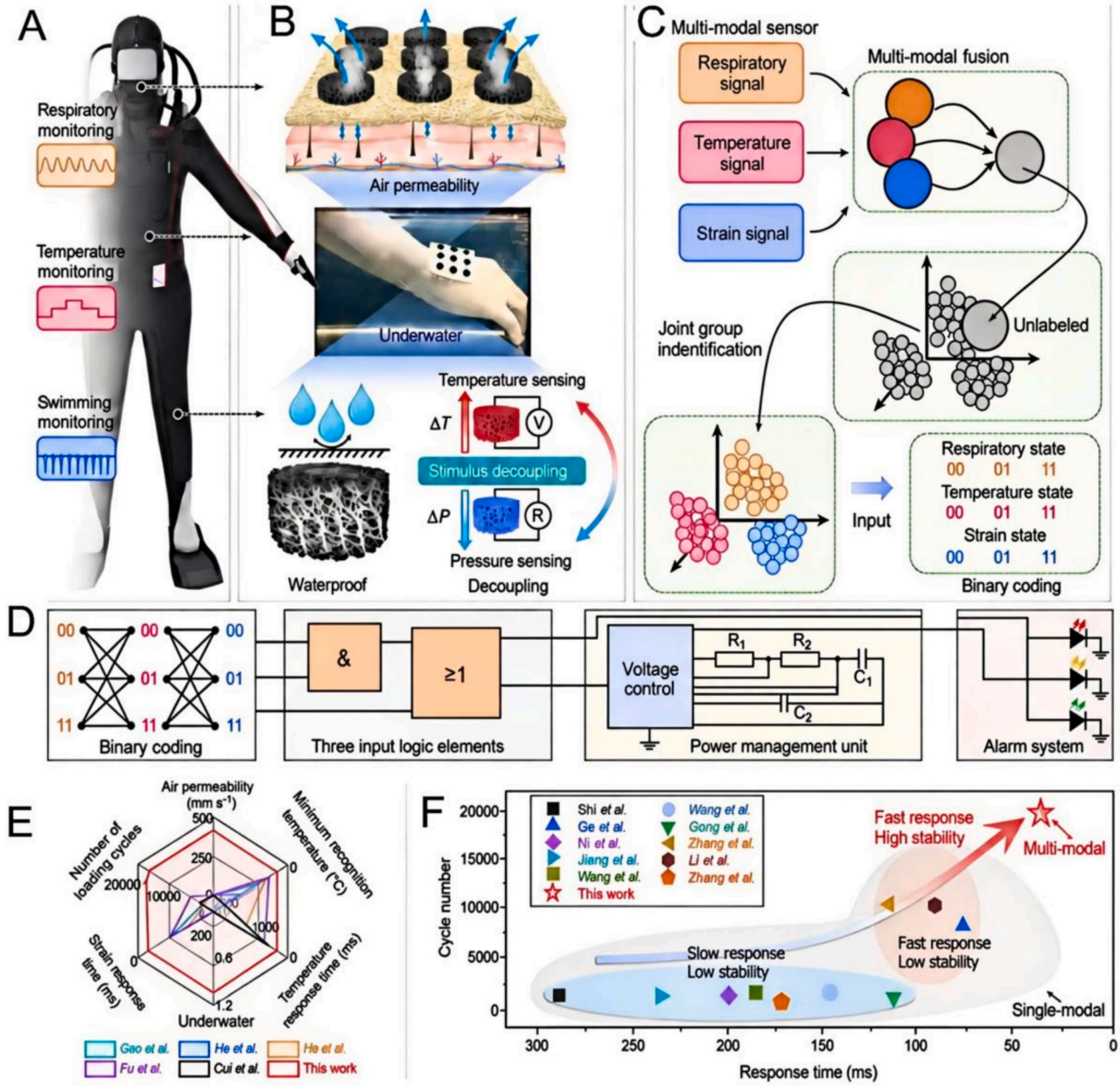


Fig. 13. Multimodal Underwater Thermoelectric Monitoring System Based on Three-Dimensional Porous Thermoelectric Foam (TEPUF). (A) Three-dimensional porous thermoelectric foam with a SWCNT/PEDOT:PSS/WPU conductive coating, simultaneously exhibiting waterproofness, breathability, and mechanical flexibility. (B) Decoupling of dual-modal temperature–strain sensing signals based on the Seebeck effect and the piezoresistive effect. (C) Application of TEPUF for underwater human-health monitoring, enabling the simultaneous detection of body temperature, respiration, and human motion. (D) Evaluation of the long-term thermoelectric stability of the device after prolonged underwater immersion. (E) Mechanical durability of the device after 20,000 cyclic compression tests. (F) Synchronous multimodal monitoring of physiological signals in complex underwater environments enabled by TEPUF. (A-F)Reproduced with permission from Ref. [19]. Copyright 2026 Springer Nature.

In terms of environmental adaptability, this class of materials achieves robust performance in extreme environments through carefully engineered chemical modification strategies. The researchers constructed a robust interpenetrating network structure through the hydrogen-bonding interactions formed between waterborne polyurethane (WPU) and the conductive polymer PEDOT:PSS. This design endowed the porous foam framework with excellent hydrophobicity, achieving a water contact angle of 112°. This design not only overcomes the longstanding issues of water-induced swelling and delamination of conductive layers that commonly affect conventional porous organic materials, but also ensures that the material maintains stable thermoelectric performance and mechanical resilience even after prolonged underwater immersion (for more than 8 h) or 20,000 cycles of repeated mechanical compression. More importantly, the hydrophobic modification of this microstructure avoids the drawbacks associated with fully sealed encapsulation. As a result, the material achieves effective waterproofing while still maintaining exceptionally high air permeability (406 mm s^{-1}). This characteristic ensures that heat and moisture exchange between the human body and the surrounding environment remains unobstructed when the material is used in wearable devices.

In terms of environmental signal monitoring, the application of thermoelectric materials has evolved beyond simple temperature sensing and is increasingly advancing toward the decoupling and simultaneous detection of multiple environmental signals. In complex

underwater environments, pressure fluctuations, water-flow disturbances, and temperature variations are often intricately coupled, placing extremely demanding requirements on the signal discrimination capability of sensing systems. The newly developed TEPUF material successfully achieves the physical decoupling of strain–pressure sensing, based on the piezoresistive effect, and temperature sensing, based on the Seebeck effect, by exploiting its unique three-dimensional porous architecture. Experimental results demonstrated that even when the material was subjected to large compressive deformations of up to 60%, the generated thermoelectric voltage signal (representing temperature) remained unaffected by changes in electrical resistance (representing pressure or motion). This finding confirms the effective physical decoupling of temperature sensing and strain–pressure sensing within the material. As shown in Fig. 13, this characteristic enables the material to function as an intelligent sensing platform capable of independently monitoring a diver's body-temperature variations, respiration rate, and limb-motion status simultaneously in underwater environments, without concern for signal crosstalk among different environmental stimuli. As illustrated in Fig. 13A, researchers employed polyurethane foam (PUF) as a three-dimensional supporting framework and uniformly deposited a conductive coating composed of single-walled carbon nanotubes (SWCNTs), PEDOT:PSS [119], and waterborne polyurethane (WPU) onto its surface, thereby constructing a three-dimensional thermoelectric foam that simultaneously exhibits excellent electrical conductivity and hydrophobicity. The porous framework retains a large number of interconnected air channels, which not only preserve the lightweight and highly elastic characteristics of the device but also maintain excellent breathability, thereby facilitating heat and moisture exchange between the human body and the surrounding environment. Meanwhile, the hydrogen-bonding network formed between PEDOT:PSS and WPU further strengthens the interfacial adhesion between the conductive layer and the polymer matrix, enabling the material to retain stable electrical conductivity even after prolonged underwater immersion and providing a reliable foundation for stable thermoelectric signal generation. Building upon its robust structural stability, Fig. 13B further illustrates the decoupling mechanism for dual-modal temperature and pressure sensing. In this device, temperature is detected through the Seebeck effect, whereas mechanical deformation is transduced into changes in electrical resistance via the piezoresistive effect. Because the two sensing signals originate from distinct physical mechanisms, temperature variations do not affect the piezoresistive response, while mechanical deformation does not influence the thermoelectric voltage, enabling the independent detection of temperature and strain [120–124]. This physical decoupling strategy effectively eliminates signal crosstalk arising from multiple external stimuli in complex environments, thereby improving the sensing accuracy of thermoelectric devices and providing a reliable foundation for underwater human-health monitoring.

Benefiting from the porous structural design and the signal-decoupling mechanism described above, the flexible thermoelectric device further enables multimodal physiological monitoring in complex underwater environments. As illustrated in Fig. 13C, researchers integrated the thermoelectric foam onto different regions of the human body, allowing the simultaneous acquisition of multiple physiological signals, including body temperature, respiration, and human motion, thereby achieving synchronous multiparameter monitoring. Compared with conventional single-function sensors, this system is capable not only of continuously generating thermoelectric signals but also of comprehensively assessing the physiological status of the wearer by integrating multiple physiological parameters. Consequently, it provides a promising solution for health monitoring in specialized environments, including underwater operations, marine exploration, and underwater rescue missions. In addition to achieving multimodal signal decoupling, practical underwater applications also require flexible thermoelectric devices to maintain stable thermoelectric output over extended periods. To this end, researchers further evaluated the long-term thermoelectric performance of the device under prolonged underwater immersion, as illustrated in Figs. 13D. Experimental results demonstrate that TEPUF maintains a stable Seebeck coefficient and thermoelectric output during prolonged underwater immersion, indicating that the conductive network formed by SWCNT/PEDOT:PSS/WPU effectively resists water penetration, thereby preventing delamination of the conductive layer and degradation of thermoelectric performance. Meanwhile, the porous framework preserves continuous heat-transfer pathways, enabling the device to maintain a stable temperature gradient even under underwater conditions and thereby ensuring reliable long-term thermoelectric monitoring [125–127]. Beyond environmental stability, flexible devices must also withstand the repeated mechanical deformation associated with human motion. Figs. 13E further presents the mechanical durability of TEPUF under cyclic compression. Owing to its three-dimensional porous framework, external stresses are effectively distributed throughout the structure, allowing the pores to undergo reversible deformation during repeated compression and recover their original configuration upon unloading [128–131]. Consequently, even after 20,000 compression cycles, the device retains a high elastic recovery ratio and stable thermoelectric output, demonstrating excellent mechanical durability for long-term wearable applications. These results demonstrate that the porous architecture not only enhances the mechanical flexibility of the device but also significantly improves its long-term cyclic durability, thereby providing a robust structural foundation for wearable underwater monitoring applications.

Building upon the material design and signal-decoupling strategies described above, Fig. 13F further demonstrates the application of TEPUF in underwater human-health monitoring. The thermoelectric foam was integrated onto different regions of the human body, including the chest, joints, and respiratory mask, enabling the simultaneous acquisition of multiple physiological signals, such as body temperature, respiration rate, and body motion, thereby achieving comprehensive multiparameter health monitoring. Because the temperature signal is generated through the Seebeck effect, whereas the motion signal originates from the piezoresistive effect, the system is capable of simultaneously acquiring multiple physiological signals in complex underwater environments without signal crosstalk [132–141]. This capability enables continuous, multiparameter health monitoring. These results demonstrate that flexible thermoelectric devices have evolved from conventional single-parameter temperature sensors into integrated intelligent platforms that combine energy harvesting, multimodal sensing, and human-health monitoring. Overall, the combination of porous structural design, waterproof conductive networks, and temperature–strain signal decoupling ensures the stable operation of flexible thermoelectric devices in complex underwater environments. As a result, flexible thermoelectric sensors have evolved from conventional single-parameter sensing devices into multimodal platforms for human-health monitoring.

Through the integration of a three-dimensional porous architecture, a waterproof conductive network, and temperature–strain dual-modal signal decoupling, TEPUF enables stable thermoelectric output and continuous human-health monitoring in complex underwater environments. Compared with conventional flexible thermoelectric devices, it not only exhibits outstanding environmental adaptability but also enables the simultaneous monitoring of multiple physiological parameters, including body temperature, respiration, and human motion, providing a promising design strategy for intelligent wearable monitoring in challenging environments.

In the TEPUF system, the SWCNT/PEDOT:PSS/WPU coating provides the electronic thermoelectric pathway, while the three-dimensional PUF framework controls flexibility, air and moisture transport, and mechanical recovery. The temperature signal is generated by the Seebeck effect, whereas compression, pressure, and motion are read through the piezoresistive response. The ionic thermoelectric hydrogels and ionogels discussed in the materials section are not direct long-term underwater demonstrations in the selected literature. They

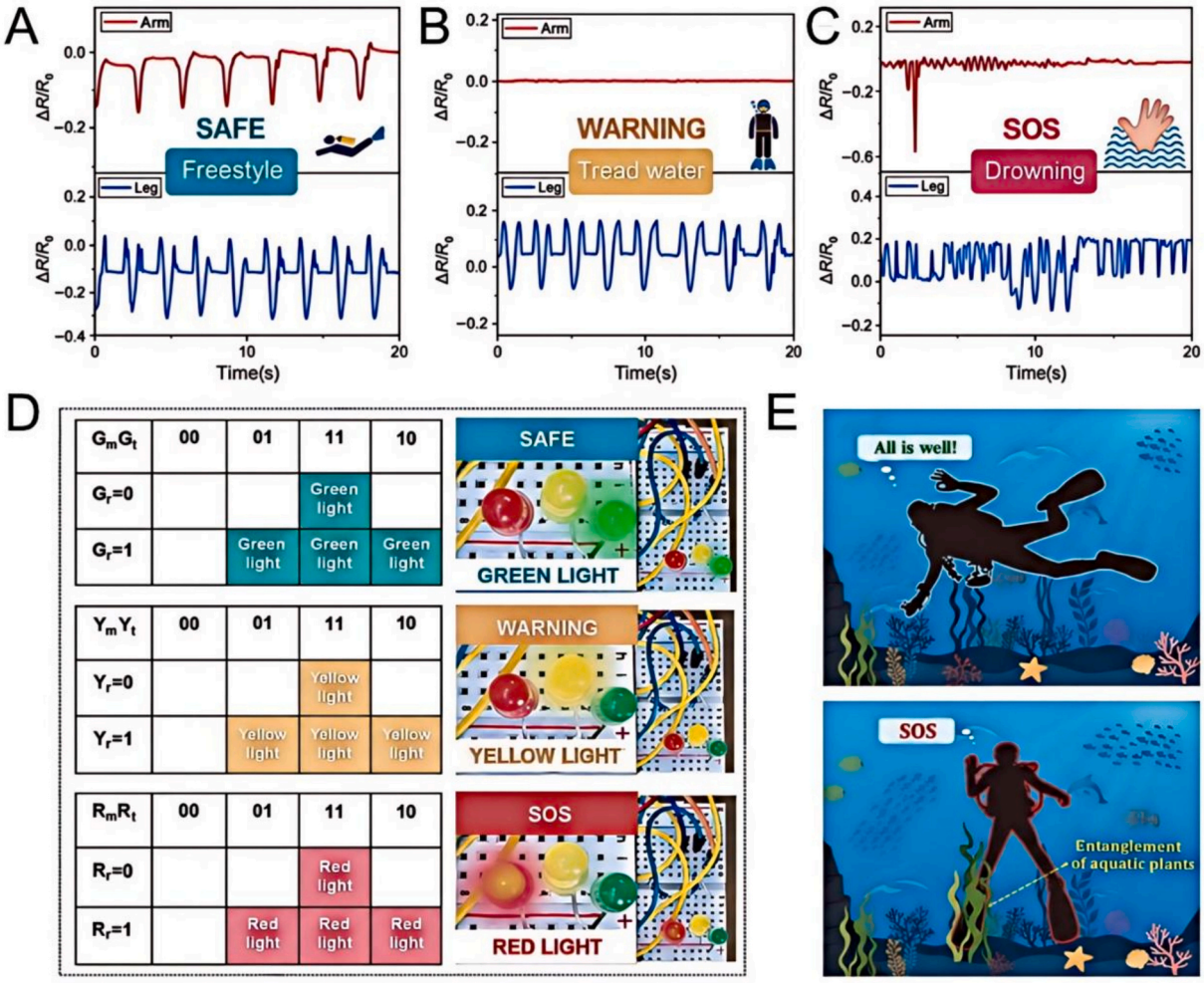


Fig. 14. Intelligent Underwater Environmental Sensing and Autonomous Early-Warning System Based on Flexible Thermoelectric Sensors. (A) Acquisition of human motion signals during normal swimming and recognition of the SAFE mode. (B) Recognition of human motion patterns during treading water and generation of a WARNING alert. (C) Identification of abnormal motion signals during drowning and activation of the SOS alarm. (D) Workflow for multimodal signal fusion and intelligent decision-making based on machine-learning algorithms and logic circuits. (E) Schematic illustration of the intelligent underwater environmental early-warning system, enabling physiological state recognition and autonomous risk warning. (A-E)Reproduced with permission from Ref. [19]. Copyright 2026 Springer Nature.

may serve as candidate compliant thermal interfaces for low-gradient sensing, but ion leaching, swelling, and signal drift under immersion require independent validation. Therefore, no unsupported ionic thermoelectric underwater case is added to this subsection. Once an individual flexible device can maintain stable operation and decouple multiple signals in water, the next step is to connect distributed nodes with data fusion, state recognition, and autonomous warning.

5.3. *Intelligent environmental sensing systems*

As discussed above, the system shown in Fig. 11 enables the simultaneous acquisition of multiple physiological signals, including body temperature, respiration, and human motion, while achieving the physical decoupling of temperature and strain signals. This capability provides a reliable data foundation for continuous human-health monitoring in complex environments. However, in practical underwater operations, multimodal sensing alone is insufficient for accurately interpreting the wearer's physiological state in real time. Effective risk assessment requires the fusion and intelligent analysis of multiple physiological signals. Consequently, recent research has increasingly integrated flexible thermoelectric sensors with machine-learning algorithms, logic-based decision-making systems, and wireless communication technologies to establish intelligent environmental sensing platforms that integrate data acquisition, state recognition, and autonomous early warning, as illustrated in Fig. 14. As shown in Fig. 14A [19], the system continuously acquires human motion signals through a distributed array of flexible thermoelectric sensing nodes positioned at different locations on the body. During normal swimming, both the upper and lower limbs exhibit stable and periodic thermoelectric response patterns, which are identified by the system as the normal motion mode (SAFE) and subsequently serve as the reference baseline for physiological state assessment. Compared with conventional single-point monitoring, this distributed sensing strategy provides a more comprehensive characterization of human motion, thereby improving the reliability of environmental monitoring [142]. As the wearer's motion state changes, the system continuously analyzes the characteristic variations in thermoelectric signals collected from different body regions. As illustrated in Fig. 14B, when the wearer transitions from normal swimming to treading water, both the movement frequency and the characteristic limb-response patterns change significantly. Accordingly, the system identifies this condition as a WARNING state. These results demonstrate that flexible thermoelectric sensors are capable not only of monitoring human motion but also of dynamically recognizing different physiological states based on

characteristic motion patterns, thereby providing a reliable foundation for risk assessment in complex environments. Furthermore, when hazardous situations such as drowning or entanglement in aquatic vegetation occur, the motion signals become markedly irregular, as illustrated in Fig. 14C. Under these conditions, the distributed sensing nodes generate abnormal thermoelectric response patterns, enabling the system to rapidly identify the wearer's condition as an SOS state and transmit the abnormal signals to the subsequent decision-making module. Compared with conventional approaches that rely on manual assessment, this strategy enables the rapid identification of hazardous conditions, thereby improving monitoring reliability in complex environments. In order to achieve automatic recognition of different physiological states, Fig. 14D further illustrates the intelligent decision-making process of the system. First, the motion, respiration, and temperature signals acquired from different sensing nodes are normalized and classified using a support vector machine (SVM) algorithm. The classification results are then converted into corresponding logical codes and processed by a logic circuit for integrated decision-making. When multiple hazard indicators simultaneously satisfy predefined criteria, the system automatically generates a three-level warning (green, yellow, or red), thereby realizing the transition from multimodal signal acquisition to intelligent decision-making. As shown in Fig. 14E, it demonstrates the practical performance of the intelligent environmental early-warning system. Under normal operating conditions, the system generates a green safety signal. When hazardous situations, such as drowning or entanglement in aquatic vegetation, are detected, it automatically switches to the red alert mode and promptly issues an early warning. These results demonstrate that flexible thermoelectric sensors have evolved beyond conventional signal-acquisition devices into integrated intelligent monitoring platforms capable of multimodal signal fusion, autonomous state recognition, and intelligent decision-making. Such systems provide a promising technological solution for continuous health monitoring and emergency rescue in complex environments.

Therefore, the development of flexible thermoelectric technologies for environmental monitoring has evolved from an early emphasis on enhancing the intrinsic performance of thermoelectric materials toward the integration of multimodal signal fusion and intelligent decision-making systems. By combining flexible thermoelectric materials, multiparameter sensing, machine-learning algorithms, and logic-based decision-making, thermoelectric devices are capable not only of continuous information acquisition in complex environments but also of autonomous physiological state recognition and real-time risk assessment. These advances provide a promising technological pathway for the development of next-generation intelligent wearable electronics and environmental monitoring systems operating in complex scenarios. In this system-level integration, electronic thermoelectric materials provide the primary sensing and signal-output pathway, whereas ionic thermoelectric materials may serve as soft, conformal thermal interfaces in future multi-node networks.

6. Conclusions and perspectives

6.1. Summary of key advances

Flexible thermoelectric sensors, based on the Seebeck effect, are capable of directly converting temperature gradients into electrical signals, thereby enabling both energy harvesting and signal sensing without relying on external power sources. Consequently, they possess significant application value in wearable healthcare monitoring, electronic skin, and complex environmental monitoring systems. This review has systematically examined the sensing mechanisms, material systems, and representative applications of flexible thermoelectric sensors. Overall, the field has evolved from its early focus on single-parameter temperature detection into a comprehensive flexible sensing platform that integrates self-powered operation, multimodal sensing, and intelligent decision-making.

In terms of materials, inorganic thermoelectric materials continue to exhibit superior thermoelectric energy-conversion efficiency. Among them, systems based on Bi_2Te_3 and Ag_2Se can effectively reduce lattice thermal conductivity and enhance charge-carrier transport performance through strategies such as nanostructure engineering, defect engineering, and interfacial design, thereby serving as an important foundation for the development of high-performance thermoelectric devices. However, inorganic materials are inherently brittle and therefore difficult to directly accommodate the requirements of human skin, textiles, or curved surfaces. Consequently, strategies such as thin-film fabrication, microstructural engineering, and integration with elastic substrates are often employed to improve their flexibility. In contrast, organic conductive polymers, carbon-based materials, MXenes, and ionic thermoelectric materials offer superior mechanical flexibility, processability, and environmental adaptability. These materials can be fabricated over large areas through techniques such as solution processing, printing, spinning, and porous-structure engineering, making them highly attractive for flexible thermoelectric applications. In particular, PEDOT, carbon nanotubes (CNTs), graphene, MXenes, and their composite systems have demonstrated outstanding performance in enhancing electrical conductivity, maintaining low thermal conductivity, and improving mechanical stability. These advantages provide a broader range of material options for the practical implementation of flexible thermoelectric sensors.

In terms of device mechanisms, flexible thermoelectric sensors are no longer limited to simple temperature-difference-to-voltage conversion. By incorporating mechanisms such as interfacial thermal-resistance regulation, deformation of porous structures, microstructural contact variation, and piezoresistive responses, thermoelectric devices are capable of simultaneously sensing multiple types of signals, including temperature, pressure, strain, respiration, and motion. Different physical stimuli correspond to different forms of electrical output, which helps reduce signal crosstalk in multimodal sensing systems and improves the reliability of data recognition. This capability is particularly important for electronic skin and wearable healthcare devices, as physiological signals on the human body surface are often characterized by low amplitude, low frequency, and susceptibility to motion-induced interference. Under such conditions, a single sensing modality is generally insufficient to meet the requirements for continuous and accurate monitoring.

In the field of biosensing, flexible thermoelectric sensors have already demonstrated considerable practical potential. By exploiting the small temperature gradient between the human body and the surrounding environment, these devices can perform body-temperature monitoring, respiration detection, pulse sensing, and localized thermal management. Some flexible thermoelectric devices can also be integrated with active cooling or heating functions, thereby forming a closed-loop system that combines energy harvesting, body-temperature sensing, and thermal regulation. The development of electronic skin has further promoted the integration of thermoelectric sensors with pressure- and strain-sensing units, enabling stable signal output during joint motion, skin contact, and tactile recognition. Beyond these functions, sweat biochemical monitoring and robotic bionic thermal perception have also emerged as important directions. Ionic thermoelectric materials are particularly attractive for sweat sensing because of their intrinsic sensitivity to ionic concentrations and redox processes, whereas electronic thermoelectric materials provide fast and stable temperature inputs for robotic thermal nociception. These examples further highlight the complementary roles of electronic and ionic thermoelectric materials in biosensing. These capabilities provide an important technological foundation for applications such as intelligent prosthetics, human–machine interaction, and personalized healthcare monitoring.

In the field of environmental monitoring, flexible thermoelectric sensors likewise offer unique advantages. In fire-warning applications, thermoelectric materials can exploit the rapidly established temperature

gradients near a fire source to generate voltage signals, enabling self-powered alarm systems and reducing the dependence of conventional sensors on external power supplies and fixed temperature thresholds. By incorporating materials such as MXenes, graphene, Ag_2Se, aramid fibers, and flame-retardant matrices, significant improvements have been achieved in high-temperature response speed, flexibility, and thermal stability. In underwater and high-humidity environments, materials such as hydrophobic porous thermoelectric foams enable the decoupled monitoring of temperature, pressure, and motion signals while maintaining both breathability and mechanical elasticity. Furthermore, when integrated with machine-learning algorithms and logical decision-making systems, flexible thermoelectric sensors evolve beyond simple signal-acquisition units and gradually become intelligent sensing nodes capable of environmental perception, pattern recognition, early warning, and assisted decision-making. This means that thermoelectric materials are no longer merely collectors of environmental information; instead, they serve as the core sensing components of intelligent systems. By continuously monitoring physiological indicators (like sudden drops in body temperature or rapid breathing) and abnormal behaviors (such as drowning-related struggles), these systems can automatically trigger graded warning responses, providing comprehensive safety protection in complex and extreme environments.

Overall, the development of flexible thermoelectric sensors has followed a relatively clear trajectory. From a materials perspective, research has expanded from high-performance inorganic thermoelectric materials toward organic-inorganic composites, ionic thermoelectric materials, and porous elastic systems. Structurally, device architectures have evolved from rigid bulk configurations to thin-film, fiber-based, foam-based, and textile-integrated formats. In terms of applications, their functionality has extended beyond single-point temperature sensing to encompass healthcare monitoring, fire warning, underwater sensing, and intelligent environmental perception. These advances indicate that flexible thermoelectric technology is undergoing a transformation from a conventional energy-conversion material platform into a multifunctional sensing platform tailored for wearable electronics and Internet of Things (IoT) systems.

6.2. Challenges, future, and development framework

Despite the remarkable progress achieved in flexible thermoelectric sensors, several critical challenges remain before their long-term deployment and large-scale commercialization can be realized. First, the trade-off between thermoelectric performance and mechanical flexibility has not yet been fully resolved. Inorganic materials generally possess high power factors and thermoelectric figures of merit, but suffer from significant brittleness and interfacial reliability issues. In contrast, organic materials offer excellent flexibility and ease of processing, yet their electrical conductivity, Seebeck coefficient, and long-term stability still require further improvement. Future research should therefore focus on achieving the synergistic optimization of performance and flexibility through multiscale structural engineering. Representative strategies include constructing continuous conductive networks using nanofillers, enhancing the Seebeck coefficient through interfacial energy-filtering effects, and mitigating stress concentration during bending by incorporating elastic matrices, porous architectures, and fiber-based structures.

Second, n-type flexible thermoelectric materials remain a major bottleneck limiting device performance. High-efficiency thermoelectric devices generally require the synergistic operation of both p-type and n-type materials. However, while the development of p-type materials in flexible systems has become relatively mature, n-type organic materials and flexible composite materials still suffer from insufficient air stability, doping efficiency, and charge-carrier transport performance. Future research should therefore focus on the development of stable n-type dopants, oxidation-resistant encapsulation strategies, and organic–inorganic hybrid architectures to improve the compatibility between p–n thermoelectric elements and enhance the overall output performance of thermoelectric devices.

Third, the long-term operational stability of flexible thermoelectric sensors requires further improvement. In practical applications, these devices are often subjected to complex conditions, including repeated bending, stretching, compression, sweat-induced corrosion, laundering, high humidity, elevated temperatures, and even direct flame exposure. The fact that a material maintains stable performance during short-term laboratory testing does not necessarily imply that it can satisfy the requirements of long-term wearability or outdoor deployment. Therefore, future efforts should focus on establishing reliability evaluation protocols that more closely reflect real-world operating conditions, including cyclic bending, tensile-fatigue testing, thermal-shock testing, hygrothermal aging, washing durability, and high-temperature flame-retardancy assessments. At the same time, encapsulation layers should not solely emphasize waterproofing and environmental isolation, but should also balance breathability, flexibility, thermal-transport pathways, and wearer comfort.

Fourth, system integration and signal-processing capabilities still require substantial improvement. The output voltage generated by flexible thermoelectric sensors is typically low and can be easily affected by fluctuations in ambient temperature gradients, body movements, and variations in contact conditions. Therefore, future device development should adopt a co-design strategy that integrates thermoelectric sensors with low-power signal-amplification modules, wireless communication units, edge-computing chips, and machine-learning algorithms. Through multimodal data fusion, the accuracy of identifying physiological abnormalities, such as abnormal body temperature and respiratory changes, as well as behavioral states, including motion patterns, fire hazards, and underwater emergency events, can be significantly enhanced. At the same time, thermoelectric devices can be combined with triboelectric, piezoelectric, photovoltaic, or flexible energy-storage units to construct multi-source energy-harvesting systems. Beyond thermoelectric devices, flexible energy-storage units can also be integrated to buffer intermittent thermal gradients. For example, flexible and twistable yarn supercapacitors based on $ZnMn_2O_4$-electrodeposited carbon yarns have demonstrated stable energy storage under repeated bending and twisting [143]. Similar flexible energy-storage units could be integrated with thermoelectric generators to buffer intermittent thermal gradients and ensure continuous operation of self-powered sensors. Such hybrid self-powered platforms can alleviate the limitations associated with unstable or insufficient temperature gradients, thereby improving the reliability, endurance, and practical applicability of flexible sensing systems in real-world environments.

Fifth, scalable manufacturing and green sustainability will be key factors in future commercialization. At present, many high-performance flexible thermoelectric devices still rely on complex laboratory-scale fabrication processes that are costly, difficult to reproduce consistently, and unsuitable for large-area, low-cost production. Future efforts should therefore focus on the development of manufacturing technologies such as inkjet printing, aerosol jet printing, screen printing, electrospinning, three-dimensional (3D) printing, and roll-to-roll processing, enabling thermoelectric functional materials to be directly deposited onto or integrated within textiles, thin films, and flexible substrates. At the same time, dependence on scarce or potentially toxic elements such as Te and Pb should be reduced. Greater emphasis should be placed on the development of sulfide-based materials, oxide thermoelectrics, carbon-based materials, bio-derived polymers, and biodegradable thermoelectric materials. Such advances will be essential for meeting the growing demands of wearable healthcare technologies and environmental monitoring systems with respect to safety, sustainability, and environmental compatibility.

Finally, the future development of flexible thermoelectric sensors should not focus solely on achieving higher *ZT* values. Instead, it should adopt an application-oriented perspective, taking into account a broader set of factors, including sensitivity, flexibility, stability, comfort,

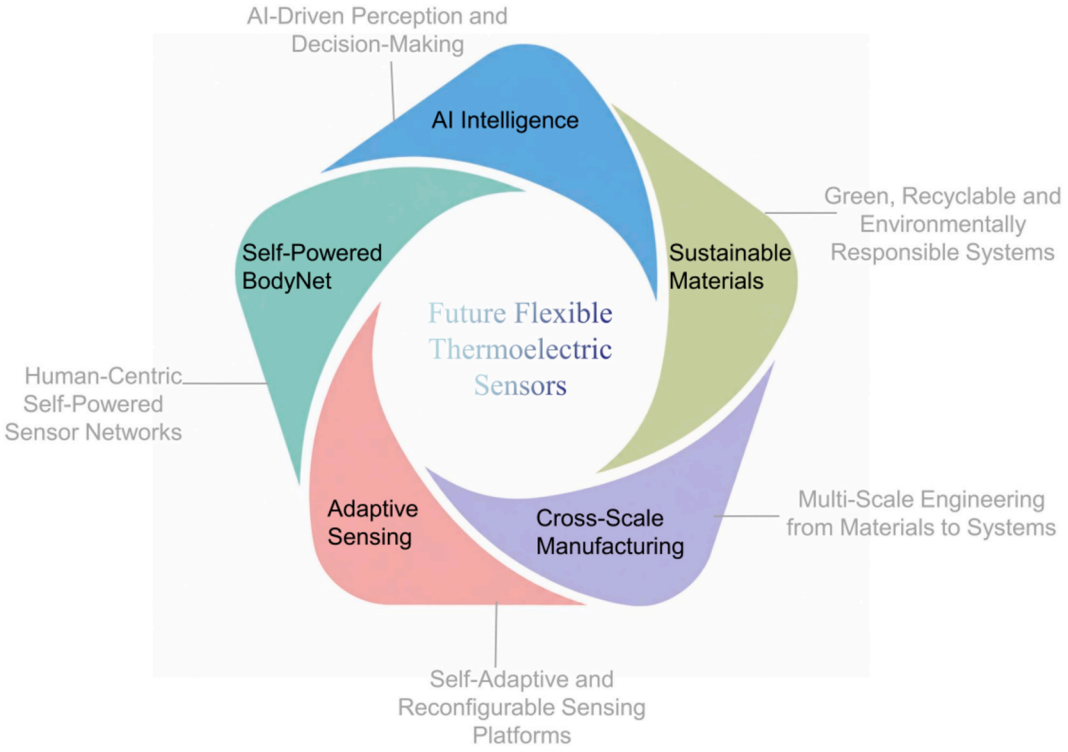


Fig. 15. Future Development Framework and Key Technological Directions for Flexible Thermoelectric Sensors.

manufacturing cost, and system-level intelligence. For human-health monitoring, priority should be given to achieving high sensitivity under small temperature gradients, together with excellent biocompatibility and long-term wearing comfort. For fire-warning and industrial safety-monitoring applications, greater emphasis should be placed on high-temperature resistance, flame retardancy, and rapid alarm capability. For underwater and high-humidity environments, key challenges include improving waterproofness, breathability, fatigue resistance, and multimodal signal decoupling.

With the continued convergence of advanced material design, flexible manufacturing technologies, low-power electronics, and artificial intelligence algorithms, flexible thermoelectric sensors are expected to progress beyond laboratory prototypes and move toward widespread real-world deployment. They have the potential to become fundamental enabling devices for future wearable healthcare systems, intelligent protective equipment, soft robotics, and Internet-of-Things-based environmental sensing platforms. To provide a more intuitive summary of future development directions for flexible thermoelectric sensors, this review further establishes a future development framework for flexible thermoelectric sensors (Fig. 15). The framework is organized around five key dimensions, such as materials innovation, manufacturing technologies, sensing capabilities, network construction, and intelligent decision-making and systematically summarizes and projects the future development pathways of flexible thermoelectric sensors. It reflects the ongoing transition of the field from standalone thermoelectric devices toward intelligent, self-powered, and multifunctional sensing systems.

As illustrated in the future development framework, continued advances in AI-enabled sensing, sustainable materials, cross-scale manufacturing, adaptive sensing technologies, and self-powered body-area networks are expected to accelerate the transition of flexible thermoelectric sensors from laboratory prototypes to practical deployment. Through the deep integration of materials design, flexible manufacturing, low-power electronics, wireless communication, and artificial intelligence, flexible thermoelectric sensors are poised to evolve into intelligent platforms capable of energy harvesting, multimodal sensing, autonomous decision-making, and real-time interaction. Ultimately, they are expected to become fundamental enabling devices for next-generation wearable healthcare systems, intelligent protective equipment, soft robotics, and Internet-of-Things environmental sensing networks, providing a critical technological foundation for the development of a more interconnected, intelligent, and sustainable future. These five development directions are not independent of one another; rather, they are mutually reinforcing and evolve synergistically across multiple levels, including materials innovation, device engineering, system integration, and intelligent algorithms. Advances in any one of these areas can stimulate progress in the others, collectively driving the development of next-generation flexible thermoelectric sensing technologies. Moreover, this development framework is broadly applicable to complex environmental-monitoring scenarios, such as fire warning, underwater monitoring, and intelligent environmental sensing, and thus provides a conceptual foundation for the future construction of Internet-of-Things (IoT) sensing networks. Through the coordinated integration of self-powered sensing, multimodal information acquisition, intelligent data processing, and wireless communication, flexible thermoelectric sensors are expected to play an increasingly important role in future distributed sensing systems, enabling more efficient, reliable, and autonomous environmental perception and safety-management capabilities.

CRediT authorship contribution statement

Yuying Wu: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition. **Yizhu Zhang:** Writing – original draft. **Xin Jin:** Resources. **Xinyuan Zhu:** Resources. **Gang Zhou:** Methodology. **Youfu Wang:** Writing – original draft. **Hao Liu:** Writing – review & editing, Writing – original draft.

Declaration of competing interest

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

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Data availability

No data was used for the research described in the article.

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