Advances in organic thermoelectric materials and devices for smart applications

Yue Zhao | Liyao Liu | Fengjiao Zhang | Chong-an Di | Daoben Zhu

School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing, China
Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

Correspondence
Fengjiao Zhang, School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China. Email: fjiaozhang@ucas.ac.cn
Chong-an Di, Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Email: dicha@iccas.ac.cn

Funding information
National Key Research and Development Program of China, Grant/Award Numbers: 2017YFA0204700, 2018YFE0200700; National Natural Science Foundation of China, Grant/Award Numbers: 21805285, 21905276, 22021002, 61971396; National Science Foundation of Beijing, Grant/Award Number: 4202077; Beijing National Laboratory for Molecular Sciences, Grant/Award Number: BNLMS201912; University of Chinese Academy of Sciences, Grant/Award Number: Y954011XX2; Chinese Academy of Sciences, Grant/Award Number: ZDBS-LY-SLH034

Abstract
Organic thermoelectric (OTE) materials have been considered to be promising candidates for large area and low-cost wearable devices owing to their tailororable molecular structure, intrinsic flexibility, and prominent solution processability. More importantly, OTE materials offer direct energy conversion from the human body, solid-state cooling at low electric consumption, and diversified functions. Herein, we summarize recent developments of OTE materials and devices for smart applications. We first review the fundamentals of OTE materials from the viewpoint of thermoelectric performance, mechanical properties and bionic functions. Second, we describe OTE devices in flexible generators, photothermoelectric detectors, self-powered sensors, and ultra-thin cooling elements. Finally, we present the challenges and perspectives on OTE materials as well as devices in wearable electronics and fascinating applications in the Internet of Things.

KEYWORDS
flexible generators, organic thermoelectric materials, self-powered sensors, smart electronics, thin-film cooling

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.
© 2021 The Authors. SmartMat published by Tianjin University and John Wiley & Sons Australia, Ltd
Smart systems trace their origin to a research field by developing materials that can mimic biological behaviors. This essential idea has been extended to various fields beyond typical bionics. For instance, integrated smart systems (ISSs), which combine multiple components to perform automated tasks, have attracted significant interest owing to their ubiquitous applications in intelligent sensors, displays, energy, and communication.1–3 To satisfy these requirements, certain materials are used that can respond to environmental stimuli and/or power electronic devices. Thermoelectric (TE) materials do not only permit energy harvesting from waste heat and solar heat but also can enable solid cooling in a reversible manner.4–6 Although the foundation of TE materials was provided through the discovery of the Seebeck effect in the early 19th century,7 TE devices have rarely been utilized as smart elements. Over the past decade, TE-material-based applications have garnered considerable attention. Two clear examples include the incorporation of TE conversion to textiles for fabricating wearable power generators and the construction of terahertz detectors, which are combined to demonstrate the promising applications of TE materials.8–13

Organic materials are considered as important TE candidates because of their diverse molecular design, good solution processability, excellent flexibility, and prominent TE performance at room temperature.14–17 These combined properties provide novel opportunities for organic thermoelectric (OTE) materials to serve as smart power generators, solid cooling devices, and sensing elements. Even though initial studies regarding the Seebeck effect of conjugated molecules have been performed a few decades ago, the development of OTE materials is slow before 2010. Recently, both OTE materials and devices have made great achievements, as evidenced by the high figure-of-merit ZT over 0.2 for both p- and n-type materials.18–22 Moreover, various OTE devices have been demonstrated as flexible power generators and self-powered pressure-temperature sensors, including those for multifunctional e-skin.16,23 Hence, a review pertaining to OTE materials-based smart applications is necessitated not only to summarize recent progresses but also to analyze the development trend of this emerging area for wide applications in wearable electronics and low-power-consumption Internet of Things (IoTs).

To date, the progress of OTE materials has been reviewed from the viewpoints of material design, chemical doping, and operating mechanism.16,18,24–28 Herein, we initiate the review with the requirements of smart devices for TE materials. Thereafter, we summarize the development of OTE materials from the perspectives of TE performance, mechanical properties, processability, and bionic properties. Thirdly, we highlight the fundamental concepts to enable flexible generators, photothermal (PTE) detectors, self-powered sensors, and ultra-thin cooling elements. Finally, we critically analyze the potential of OTE-based smart electronics in both material and device engineering.

### 2 | Fundamental of OTE Materials for Smart Devices

OTE materials enable the direct conversion between heat and electricity via the Seebeck and Peltier effects in a reversible manner (Figure 1). The Seebeck effect is a typical TE phenomenon that is used to convert a temperature difference to an electric field.29–31 Seebeck coefficient (S) is defined as $S = \Delta V / \Delta T$, where $\Delta V$ and $\Delta T$ are output voltage and temperature difference, which provide a comprehensive insight into the energetics of the dominant charge transport process and is determined by the characteristics of the band structure and scattering events. In contrast, the Peltier effect
occurs when the current flows through an isothermal junction between two materials.\textsuperscript{12-34} Hence, another fundamental TE parameter (Peltier coefficient) is referred to describe current ($I$) induced energy diffusion via the expression $\frac{dQ}{dt} = (\Pi_2 - \Pi_1) \times I$, where $dQ/dt$ is the rate of heat generation, $\Pi_2$ and $\Pi_1$ are the Peltier coefficients of the two materials. Notably, the Thomson relation interrelates the Seebeck and Peltier coefficients and can be described by $\Pi = S \times T$, where $T$ is the absolute temperature.\textsuperscript{35} For TE conversion, the efficiency is determined by the figure of merit ZT, which is expressed as $ZT = S^2 \sigma / \kappa$, where $\sigma$ and $\kappa$ represent electrical conductivity and thermal conductivity, respectively. Notably, the power factor $PF = S^2 \sigma$ is also frequently used to evaluate TE performance.

Based on the aforementioned effects, OTE materials can be utilized in different ISSs as follows. First, TE materials hold the capability of transforming a heat flow into electricity, thereby allowing the electronic devices to be driven in an alternate route. Second, the Peltier effect of TE materials offers a unique method for cooling electric devices. Third, OTE materials can be designed to possess external chemical/physical properties, which enable multifunctional TE candidates for wearable, flexible, and implantable applications. In this section, we attempt to summarize the requirements of smart devices for OTE materials.

### 2.1 High TE performance

A high ZT value can ensure superior power generation and Peltier cooling efficiency. For smart applications such as wearable electronics and IoT, ZT values at room temperature are vital to energy supply. So far, the commercial materials typically exhibit ZT values of 0.6–1.\textsuperscript{36} By contrast, few OTEs have been reported to possess ZT values exceeding 0.1, primarily because of the limited material categories and unsatisfied doping methods. Herein, we describe several p- and n-type OTE materials with ZT over 0.1, which hold the potential for intelligent applications.

Early research regarding OTE materials has been limited to p-type conducting polymers such as Poly(3,4-ethylenedioxythiophene) (PEDOT) (Figure 2).\textsuperscript{37} PEDOT is always emulsified with polyelectrolytes, such as poly(styrene sulfonate) (PSS) and tosylate (Tos), in water, because of its poor solvent solubility. Its TE properties can be manipulated via fine-tuned doping with organic solvent or vapor.\textsuperscript{38} In 2011, Crispin et al.\textsuperscript{39} demonstrated a strategy with accurate control of the oxidation level of PEDOT:Tos, for which the films were reduced using tetrakis(dimethylamino)ethylene vapor. The power factor of the thin films can reach 324 $\mu$W/(m·K$^2$) at an oxidation level of 22%, with a maximum ZT value of 0.25 at room temperature. PEDOT:PSS has reported a ZT value up to 0.42 at room temperature by mixing DMSO.\textsuperscript{21} Since 2012, Zhu et al.\textsuperscript{18,19,40} reported a series of coordination polymers with transition metal ions and ethylenetetrathiolate (ett), which exhibit outstanding TE performance. As an example, poly(nickel-ethylenetetrathiolate) (poly(Ni-ett)) exhibited a ZT of 0.2 at 400 K.\textsuperscript{40} Moreover, the same group developed more ordered poly(Ni-ett) films via electrochemical deposition.\textsuperscript{19} The obtained film indicated a high PF over 100 $\mu$W/(m·K$^2$) and a maximum ZT value of 0.30 ± 0.03. These reports represent early examples of high-performance OTE materials based on conducting polymers.

Chemically doped organic semiconductors (OSCs), such as poly(3-hexylthiophene) (P3HT), poly(2,5-bis(3-dodecyl-2-thienyl)thieno[3,2-b]thiophene) (PBDTTT), and diketopyrrolopyrrole polymers (PDPPs), are alternative category of OTE materials.\textsuperscript{41} Despite hundreds of high mobility OSCs reported previously, few have been demonstrated as OTE candidates. To date, DPP-based and DPP-like derivatives have been reported as promising OTE materials with chemical doping treatments.\textsuperscript{22,42,43} We reported a high-performance selenium-substituted DPP derivative, PDPPSe$_{12}$.\textsuperscript{22} Notably, selenium substitution contributed to a stronger intermolecular interaction, enabling high carrier mobility and an ordered molecular packing after doping treatments. Consequently, a conductivity larger than 900 S/cm and an $S$ of 62.3 $\mu$V/K, resulting in a maximum PF and ZT of up to 364 $\mu$W/(m·K$^2$) and 0.25, respectively. DPP-based small molecules are excellent OTE candidates. Chemical-doped DPP materials with different donor units exhibit a high electrical conductivity over 1 S/cm.\textsuperscript{44} By incorporating aromatic structures into dipyrrolo-[3,4-c]pyrrole-1,4-diyldenedibis(thieno[3,2-b]thiophene) (DPPTT),\textsuperscript{43} we demonstrated that A-DCV-DPPTT possesses optimized energy levels and high electron mobility. Moreover, the molecular stacking and dopants aggregation in solid films resulted in a significant polarity difference between the OSC and dopant 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyl)dimeethyl amine (N-DMBI). Consequently, an efficient electron transfer was enabled between A-DCV-DPPTT and N-DMBI$^*$, resulting in a maximum PF of up to 236 $\mu$W/(m·K$^2$), as well as an excellent ZT of 0.23 ± 0.03. Recently, Liu et al.\textsuperscript{20} demonstrated a molecularly n-doped fullerene derivative with high TE performance by applying the concept of “phonon-glass electron-crystal.” Through the meticulous design of the molecular structure of fullerene derivatives, the author revealed a thermally stable N-DMBI-doping and disorder-to-order transition upon the annealing of the fullerene molecule with double-triethylene-glycol-type side chains. In this case, an organic electron
crystalline film with a $\sigma$ more than 10 S/cm was formed a low $\kappa$ less than 0.1 W/(m·K), leading to the highest ZT of 0.34.20

2.2 | Fine-tuned mechanical properties

To promote the sustainability of OTE materials for wearable devices, fine-tuned mechanical deformation tolerance is urgently required. Generally speaking, wearable devices demand tissue-like mechanical properties to enable their seamless integration with the human skin. Core parameters that must be considered include Young’s modulus, bending radius, and elastic properties. First, Young’s modulus of the materials and devices should be lower than that of the attached position.45 For instance, Young’s modulus of ideal OTE materials should be less than 1 GPa for wearable clothing, where it should always be in the range of 25–220 kPa for skin-attached application.46 Based on the abovementioned methods, several groups have developed novel OTE composites and gels by introducing stretchable polymer semiconductors to elastomer/insulators. For instance, Müller et al.
reported flexible OTE materials composed of a stretchable semiconductor/insulator blend that yields a high tensile strain of 100%. Jang et al. also employed triblock copolymer to modulate the elastic properties of a ternary OTE material with a ZT value of 0.00126. In addition, OTE devices can be integrated with a free-standing film or an active matrix made of polymer insulators poly(dimethylsiloxane) (PDMS), poly(vinyl alcohol), paper, and fibers, thereby confirming their applications in bendable and wearable attachment requirements.

### 2.3 Solution processability

The solution processability of organic materials is key for realizing low-cost and large-area applications. For instance, in OTE materials, emphasis should be directed toward overcoming the challenge of printing high-performance devices with high resolution. Consequently, issues will be encountered in the development of suitable printing techniques and TE inks. In terms of printing methods, inkjet printing, slot die, and roll-to-roll fabrication contribute to continuing deposition. To achieve high resolution and patterned TE samples toward efficient energy conversion, strategies including well-designed integration structure, surface modification, and soft mask, have been developed for solution fabrication. Moreover, the OTE ink consists of OTE solution or gels. Hence, both the components and viscosity should be optimized to manipulate the uniformity, morphology, and TE properties. The dopants can be printed simultaneously or subsequently using intrinsic OTE materials to create patterned p-legs and n-legs, which are typically used in woven and wearable TE textures.

In addition, OTE materials can be deposited via the electrochemical method. For instance, PEDOT and poly[K$_n$(Ni-ett)], can be electrochemically deposited to fabricate large-area film with high performance because of the fine-tuned doping level during the continuous deposition. To realize the electrochemical polymerization of OTE materials, the reaction mixture should be composed of a TE precursor and water-soluble polyanions/polyca-

### 2.4 Bioinspired functionalities

In recent years, a host of bioelectronics has been designed and fabricated to fulfill the requirements of healthcare and lifestyle. An important trend and open issue pertaining to OTE materials is the method to endow these materials with bionic features such as self-healing, as well as artificial perception functionality. From the perspective of self-healability and recyclability, the chemical structure and assembly structure design of OTE materials have garnered increasing attention. Therefore, heating-cooling aggregation features, dynamic bonding reactions in the corresponding supramolecular systems, and additional capabilities enabled by adding supplementary healing agents have been demonstrated for bioinspired smart systems.

To develop OTE-based bionic devices, the materials to be used are recalled with multifunctionality. For instance, we developed a printed e-skin based on microstructure-frame-supported organic thermoelectric (MF SOTE) materials, which incorporate piezoresistive property with TE property. Moreover, self-powered artificial intelligence in implantable healthcare requires TE materials and devices to exhibit biocompatibility in complex environments, they can be degraded via chemically and/or enzymatically induced hydrolysis and oxidation. In this case, novel OTE materials are encouraged to be designed to disintegrate into natural or bio-derived units as well as multifunctional units. These bioinspired functionalized OTE materials have enabled a more seamless integration of devices with irregular, deformable, or dynamic systems, particularly the human body.

### 3 Flexible Devices and Smart Elements Based on OTE Materials

By virtue of the significantly improved performance of OTE materials, several integrated devices have been developed to demonstrate their applications in different areas. In this section, we describe OTE devices for multiple applications including OTE generators (OTEGs), PTE detector, self-powered sensors, and thin-film cooling applications. Several key strategies for constructing intelligent devices are summarized to facilitate their further integration into ISSs.

#### 3.1 Flexible OTEGs

From the point of power consumption, the existing electronic devices can be classified into four groups, including high power (≥10 W), medium power (1–10 W), low power (1 mW–1 W), and ultra-low power (≤1 mW).
Limited by the low-temperature difference in wearable and IoT systems, OTE devices are likely to be suitable for ultra-low power consumption (≤1 mW) as well as self-powered devices. Accordingly, existing studies regarding OTE devices focus on: (i) obtaining higher ZT value and low internal resistance of the TE leg to facilitate a higher thermal output power, (ii) optimizing the integration structure and density to increase the output voltage with logic circuit design, (iii) endowing the device with an easier fabrication process, good flexibility and excellent stretchability.

Most OTEGs with high output energy reported to date are based on materials with high ZT, including doped PEDOT and poly[An(M-ett)]. Crispin et al. reported a TDEA-treated PEDOT:PSS solution that afforded high TE conversation ability, with a maximum ZT of 0.25. Combining with the inkjet deposition of PEDOT:PSS and tetrafluorovulene-tetracyanoquinodimethane to fill SU-8 cavities to form the p-legs and n-legs, respectively. They demonstrated an OTEG comprising 54 legs with an electrical power of 0.27 μW/cm² at ΔT = 30 K. Zhu et al. reported a series of metal coordination poly[An(M-ett)] with a good ZT value higher than 0.2. Poly[Na(Ni-ett)] and poly[Cu(Cu-ett)] were selected to construct a 35 n-p couples TE module, which can yield an output voltage of 0.26 V and a power of 2.8 μW/cm² at ΔT = 80 K. They further demonstrated a flexible OTEG by employing a 5 mm thick PDMS membrane to create 440 units with bulk samples with a size of 1 x 2 x 5 mm (Figure 3A), which yielded an output voltage and current of 1.51 V and 2.71 mA, respectively. A suitable output power successfully drives a calculator independently (Figure 3B). In 2017, researchers constructed flexible OTEGs via electrochemical deposition (Figure 3C). In this process, a PDMS template was printed on a polyethylene terephthalate (PET) substrate as a mask, resulting in a prototype unipolar TEG with a series connection. The 108 legs shown an average Seebeck coefficient of −153 μV/K, and an average power density of 300.3 μW/cm². The devices displayed a steady output voltage of 25 mV in response to a temperature difference of 12 K, corresponding to the stable performance of the OTE materials. For smart devices, the output voltage can be easily created by the temperature difference between the body and the environment. However, compared with the aforementioned bulk generators, the heat-flow direction of this thin film should be controlled along the TE stripe between two electrode ends (constant ΔT for all legs), or two ends of the TEG path (different ΔT from top to bottom rows), bringing a challenge for their application in wearable devices. Hence, a device with a thin-film architecture is developed by employing an “electrode-OTE thin layer-electrode” sandwich structure or a roll-to-roll printing structure. Krebs et al. reported a p-type unipolar TEG achieved via roll-to-roll printing, which contained 18,000 serially connected junctions of Ag/PEDOT:PSS/Ag on a PET substrate. The array can be rolled up into a cylindrical structure to support the vertical temperature gradient when attached to any object. Lucas et al. further created an n-p prototype via in situ oxidative polymerization and intercalation of PEDOT on a paper substrate with V₂O₅·H₂O. As shown in Figure 3D, the optimized geometry of the OTEG can yield a maximum power output of 0.34 nW at ΔT = 20 K (four legs).

Another widespread approach for personal electronic devices based on OTEGs is integrating a power generator with textile fabric. This method can not only convert the surrounding energy into electrical energy, but also enable the use of comfortable, breathable, nontoxic, and washable fabric. In this case, the designed OTE fabric should be endowed with a TE power generating function, and the fabric permeability should be unchanged. Lin et al. firstly demonstrated a flexible and air-permeable TE energy harvesting fabric based on PEDOT:PSS coated a commercial fabric. The fiber surface was covered evenly with PEDOT:PSS via immersing process, thereby supporting the stable TE properties. Experimental results obtained by attaching the OTEG fabric onto adult skin, demonstrated a flexible and comfortable clothing generator. This five TE-strip generator can yield a maximum power of 388.7 μW based on the temperature difference between the skin and the ambient temperature. Interestingly the breathable feature of the fabric was maintained (or increase slightly) because the PEDOT:PSS solution compressed the yarns during the coating process. It should be noted that the fabric strips were connected with metal electrodes. In comparison, Park and Kim et al. developed a robust clothing generator based on all-carbon nanotube yarn (CNTY). The yarn was first immersed into a carbon nanotube (CNT) solution, and subsequently doped with polyethyleneimine and FeCl₃ as n- and p-type dopants, respectively. A CNTY with 60 n-p pairs yielded a maximum power density of 10.85 and 697 μW/g at a ΔT of 5 and 40 K, respectively. The fabric-assembled TE modules were able to power multitudinous wearable electronics under body heat, whereas the invalid two-dimensional architecture of the fabric limited its application because of low energy harvesting. In 2019, Zhang et al. developed a spacer fabric-shaped three-dimensional (3D) TE textile on a large scale, using a matured industrial textile process. They studied the TE harvest performance of various fabric OTEGs by finite element simulation and experimental analysis, interestingly, demonstrating a textile structural effect of CNTY in practical application. The optimized flexibility and stability OTEG displayed a high output power density of 51.5 mW/m² at a ΔT of 47.5 K. Sun et al. also demonstrated a stretchable 3D TE generator by weaving the fibers into π-type TE modules. As shown in Figure 3F, the CNT fiber-based module was first developed via
FIGURE 3 (See caption on next page)
oleamine doping combined with electrospray technology, and then interlocked in a 3D-pattern structure without substrates. The TE generator is capable of sufficient alignment with the heat flow and excellent stretchability, which was successfully constructed as a wearable cloth (Figure 3G). In this case, the integrated TE generator supplied a superior power density of 70 mW/m² at 44 K (Figure 3H). With more efforts devoted to developing OTE-based integrated devices, their physical and chemical properties have been further modified to enable a functional TEG, such as the fluoropolymer-incorporated fabric TE generator that renders the device hydrophobic, thereby improving the washability.

Currently, self-healable devices have resulted in the development of novel wearable elements, which require robust and stable output power under external mechanical stresses. Most OTEGs are stretchable owing to their intrinsic flexibility but are mechanically brittle or affected by unrecoverable properties after being subjected to damage. Hence, several groups have developed novel TE materials based on material structure design, ternary composite, and fabrication technologies. For instance, Jang et al. demonstrated self-healable and stretchable OTE materials by embedding conducting polymer nanowires in a thermoplastic elastomer matrix. The TE properties of the matrix can be modulated by changing the concentration of P3HT and tris(pentafluorophenyl) borane (BCF) in a polystyrene-block-polyisoprene-block-polyisoprene (SIS) copolymer (Figure 3I). More importantly, the “cutting, healing, and stretching” test performed on SIS/P3HT/BCF composite before and after various treatments indicated that the composite OTEG exhibited self-healing properties under mild heat and pressure (Figure 3J). These functionalities render TE harvesters effective for powering artificial electronic skins and wearable devices. Baran et al. also developed a 3D printing method for self-healable OTEGs, the results of which indicated good deformability and repetitive cutting/self-healing qualities. These strategies represent a significant step forward with wearable power generators with the advantages of a long operating lifetime, easy maintenance, high reliability, and environmental friendliness.

Given the aforementioned advantages of flexible OTEGs, many groups have developed OTE materials integrated with different devices. Crispin et al. introduced ion transport to enable new functional devices. Compared with the electron/hole Seebeck coefficient for conducting/semiconducting polymers, the ionic TE Seebeck coefficient of polymer electrolytes can reach 10 mV/K. Therefore, the ion TE generators can power the ion-gated effect transistor as well as support an outstanding sensing amplification in a single TE leg (Figure 4A,B). Owing to the signal transition and energy conversion properties, they successfully developed a heat-gated logic inverter (Figure 4C), thereby contributing to the realization of larger and more complicated circuits. Meanwhile, we created OTEG-dependent electronic sensors by integrating thin-film organic TE legs on a paper substrate, which can support an output voltage of 52.3 mV for a skin-attached OTE array (Figure 4D). Integrated with a sensing OFET with ultralow power consumption, the paper-based OTEG can drive a sensitive ammonia sensor for long-term operation, facilitating the construction and application of ISSs. It should be noted that the OTEG, which features excellent durability and biocompatibility, is garnering increasing attention for future smart electronics.

### 3.2 PTE detector and power generator

For TE materials, light irradiation can affect the TE conversion via photo-thermo-electric (P-T-E) or photothermoelectric (P-T-E) effects, which causes an additional photothermal energy conversion or photoinduced...
excitation on the transport carriers of the active materials, respectively. Benefiting from these PTE effects, the photons can be converted to electric signals, making the TE materials promising candidates for photodetection and photoelectric generators. In this section, we will focus on the OTE‐based light detector, and provide an alternative application of light‐assisted power suppliers.

By utilizing the advantage of light absorption from the UV/Vis range to near‐infrared (NIR) range, TE materials have been applied in various applications such as night vision sensors, security cameras, spacecraft thermal controls, and optical attenuators. The early investigations were primarily on inorganic materials, which are limited by their photothermal properties, convertible optoelectrical properties, and molecular designs. The developments of OTE with easy processability, excellent flexibility, and optimized performance have stimulated the studies pertaining to PTE detectors. Kim et al. developed a new material hexyl‐3,4‐ethylenedioxythiophene (EDOT‐C6) with electrochromic and PT properties. Based on the convertible absorption between the visible and NIR regions for the neutral and doped states, PEDOT‐C6 can be used for light detection (Figure 5A). In this case, the doped thin film is visible to the NIR laser, which induced a temperature increase and voltage generation by maintaining a consistent Seebeck coefficient. As shown in Figure 5B,C, the output voltage of the OTE array driven by a hot plate and a cooling fluid, and the current response to 1 ppm ammonia of an OFET sensor powered by the OTE array. Reproduced with permission. Copyright 2019, Wiley‐VCH Verlag GmbH & Co. OTE, organic thermoelectric; P3HT, poly (3‐hexylthiophene)
exhibits strong absorbance in the NIR region (Figure 5D). More interestingly, when the NIR laser spot is located at the electrode/active layer interface, the maximum PTE voltage will be generated due to the simultaneous interface-located P-TE and P-T-E effect. After the optimization of the device structure, the poly[Cu₅(Cu-ett)]:PVDF-based devices can respond to NIR light with an intensity ranging from 1.7 mW/cm² to 17 W/cm² (Figure 5E), and a fast response time (<30 μs). These excellent sensing performances enable the detection of randomly moving NIR laser at a distance of 1.5 far away from the device (Figure 5F).

The technique developments stimulated the fascinating application of mid-NIR and terahertz (THz) waves in physical imaging.

**FIGURE 5** (A) Schematic illustration of a PEDOS-C6 based NIR detection via photo-thermal effect. (B) Seebeck voltage under various NIR laser intensities and (C) Cyclability of the TE device to a NIR laser with an intensity of 2.33 W/cm². Reproduced with permission92: Copyright 2013, Wiley-VCH Verlag GmbH & Co. (D) Photographs of NIR detectors on glass and PET substrates. (E) PTE voltages of the poly[Cu₅(Cu-ett)]:PVDF-based film device, which are generated from NIR irradiation as a function of layer power. (F) PTE voltage of the flexible detection when a 400 mW/cm² NIR (808 nm) was moved randomly away from the detector in a distance of 1.5 m. Reproduced with permission: Copyright 2015, ACS Publications.93 (G) CNT-based THz device structure and corresponding THz response map obtained by scanning the THz laser spot at 29 THz. (H) THz imaging of a metal and a piece of chewing gum concealed behind opaque objects. The images were acquired under 0.14 and 1.4 THz waves, respectively. Reproduced with permission: Copyright 2016 Springer Nature.12 CNT, carbon nanotube; NIR, near-infrared; PTE, photothermoelectric; PVDF, polyvinylidene difluoride
material composition detection, security testing, and high-data-rate communication. The TE materials have been further developed for use in correlated PTE detectors in terms of the PTE effect at the interface between different materials, such as graphene-metamaterials, graphene single-bilayer interface junctions, CNTs electrodes, and phosphorus device with asymmetric metallization. Zhang et al. demonstrated a sensitive NIR and THz photodetector based on the photoelectric phenomenon that appeared in CH$_3$NH$_3$PbI$_3$(MAPbI$_3$) and PEDOT:PSS hybrid composite with wide absorption range, large light absorption coefficient, and good electrical properties. The device exhibited a stable and repeatable response to 1064 nm and 2.54 THz irradiation at room temperature. Furthermore, Oda and Kawano reported a flexible and wearable THz scanner based on macroscopic CNT films, owing to its ability to effectively absorbing THz waves over a broad range. As shown in Figure 5G, the CNT-based device can realize a spatially resolved measurement of THz signals. Hence, the author realized THz imaging, using this scanner based on various
sample configurations that hindered obstructions under different THz waves (Figure 5H), in a simple, noncontact, and nondamaged manner. The developed wearable and portable THz scanner will enable the further development of noninvasive inspections for a variety of purposes, opening a new route towards smart monitoring applications such as medical release.

Meanwhile, light irradiation can facilitate energy harvesting owing to the photothermal-electricity conversion and manipulated TE properties. In 2020, our group realized enhanced TE performance of n-type OSCs modulated by a phototransistor. The coupled electric-field effect and light irradiation contributed to an improvement of more than 500% in terms of the PF of NDI-DTYM2, achieved by fine-tuning the exciton separation, charge screening, and carrier recombination. The TE phenomenon can be introduced to photovoltaic devices such that they can function as large power suppliers. We expect more coupling-effect studies to be conducted to boost the possible application of OTE materials and devices in smart IoTs.

3.3 Self-powered sensors

OTE materials and devices are effective power elements in a single or integrated system, enabling self-powered operation driven by environmental temperature differences. OTE-based temperature sensor constitutes the largest proportion of self-powered applications, based on the mechanism of TG generators. In these devices, the output voltage is created by the temperature gradient across the device (ΔT = ΔV/S), which can give a real-time temperature when fixed the temperature of one electrode end. As shown in Figure 6A, Wang et al. fabricated a self-powered temperature sensor based on a Te nanowire/P3HT composite. The composites indicated a positive Seebeck coefficient, which contributed to a linear relationship between the output voltage and temperature at two ends of the devices. Hence, the skin-attached OTEG can respond to a cooler that is in contact with the outer surface of the generator, which corresponds to the change in output current signal. Furthermore, the OTEG can be fixed to detect the environmental temperature change of exhaled air from the human lung (Figure 6B). The sensitive and reproducible temperature response signals enable the self-powered OTE device for healthcare monitoring. Compared with pure OTE materials, composites always exhibit functional properties. Jeon and Bae et al. employed a ternary compound ink containing PEDOT:PSS, Ag nanoparticles, and graphene, to construct a highly stretchable and wearable textile-based self-powered sensor (Figure 6C). The well-designed, patterned p-n leg overlapping structure contributes to the sensitive temperature detection because the junction was in contact with the heat source for TE voltage generation. Therefore, stencil printing with composite ink can be used for large-area sensing array construction (Figure 6D). A wearable device can be used to achieve self-powered temperature mapping. Wang and Tokito et al. fabricated a high stable temperature sensor by introducing a crosslinker (3-glycidoxypropyl)trimethoxysilane and CYTOP to passivate the vapor effect. The cross-linked P3HT device exhibited a constant high sensitivity of ~0.77 °C−1 in the temperature range between 25°C and 50°C, and the humidity changed from 30% RH to 80% RH. The excellent sensing properties attributed to the use of smart chips for the real-time monitoring of temperature fluctuations in the human body and environment (Figure 6E,F).

Self-powered multifunctional sensors are composed of a temperature sensor based on the TE effect and other physical/chemical sensors, based on the functionalized OTE compounds. In 2015, we first revealed simultaneous temperature-pressure detection using a novel concept of microstructure-frame-supported OTE (MFSOTE) materials. Figure 7A illustrates the sensing mechanism of the dual-parameter sensor, for which the conductivity and output voltage can be independently controlled via piezoresistive and TE effects, respectively. The MFSOTE device can serve as self-powered electronics once a small temperature difference is available. Therefore, the device can recognize the pressure changed to a series of gentle finger touches (Figure 7B) with power generation driven by the temperature difference between the environment and finger. Smart intelligence can be further demonstrated by the flexible, highly integrated, and sensitive MFSOTE array (Figure 7C), which was constructed via inkjet printing. The 1350 pixels in a 2 × 3 cm² area resulted in spatially resolved pressure and enabled temperature information acquisition for the wearable intelligent elements of artificial robotics and healthcare products. This concept is further developed for dual-parameter and triple-parameter sensing. For instance, Ha et al. reported a skin-like stretchable array by employing multi-walled CNT/polyaniline nanocomposite to coat the polyurethane foam. The designed materials and fabrication treatment enabled the array to be mechanically stable under stretching, bending, and twisting deformations (Figure 7E). In contrast to previous reports, this microporous structure of the conductive nanocomposite also makes it possible to respond to ammonia because of the features created by polyaniline selection (Figure 7F). More importantly, the demonstrated stretchable sensor enables skin-attachable smart chips in healthcare.
With the rapid development of mass-produced ISSs that incorporate multiple electric components, higher requirements are imposed for the effective acquisition and distinction of the multiple stimuli of smart and self-powered sensors. Problems such as long-time operation stability in ambient conditions, self-healing capability of the large-area array, and biocompatibility for implantable electronics remain to be solved. PEDOT:PSS is a representative material for bionic applications because it can support both ion transport and carrier transport in the material. However, ion transport will be significantly affected by humidity in the environment (Figure 8A,B), which consequently alters the ion TE properties (both the ion conductivity and Seebeck coefficient). A smart design by integrating a MOF-801/hydrogel self-humidifying bilayer to protect the sensor is developed, which can be used to modulate the absorption moisture and water amount subjected to the device by controlling water release and maintenance (Figure 8C). Using this design, the PEDOT:PSS-based sensor can provide constant relative humidity and output voltage ($V_{oc}$) over 72 h under various ambient conditions (Figure 8D). The ionic TE materials contribute to the fascinating investigation of multifunctional sensing and bioelectronic electronics due to the ion transport properties. Further investigations should be performed to improve...
environmentally sustainable self-powered sensors in different environments.

3.4 Thin-film cooling device

Similar to the traditional functions of OTE materials enabled by the Seebeck effect, organic TE cooling systems possess unique advantages such as compactness, light weightiness, and high reliability etc. Even though OTE-based generators and sensors have been extensively used in flexible and wearable devices, the TE cooler (TEC) remains inaccessible because of complex effect factors such as electron-electron and electron-phonon interactions, material thermal and electrical conductivities, molecular size effect, and film configuration. When designing a thin-film cooling device, Joule heating through the entire device must be considered. As reports pertaining to organic TE-based solid-cooling applications are limited, we will introduce the accomplished inorganic Peltier coolers to solid-state cooling based on OTE materials in this section.

When an electrical current flows across an isothermal junction of two materials, refrigeration will occur at one contact dependent on the current direction and the sign of the Peltier coefficient. Commercial Peltier coolers have been developed for daily lifts. However, methods to increase their cost-effectiveness, integration density, and cooling efficiency are highly demanding. In microthermoelectric (μ-TEC) modules, electricity can be used to generate cooling to manage heat locally; this aspect is critical in a range of emerging systems, such as fast temperature-controlled lab-on-a-chip devices, biomedical devices, and IoT devices. Li et al. demonstrated an integrated μ-TEC module with a packing density of 5500 leg pairs/cm². The device was constructed using a cost-effective fabrication approach, that is, via the electrochemical deposition of bismuth tellurium, which allows a large-area fabrication. The best results indicated a rapid response time of 1 ms, maximum reliability of

**FIGURE 8** (A) Schematic illustration of electronic and ionic transfer in high-doped PSSH (HDH) film at different humidity (RH). (B) Thin films ion conductivity and Seebeck coefficient as a function of PSSH content and different RH. (C) Photograph and schematic illustration of the self-humidifying TE prototype composited of a MOF-801, polymer hydrogel layer, PI spacer, and PET substrate. The left graph describes the moisture absorption, release and maintenance process. (D) The stability of the generated thermovoltage and RH information with the self-humidifying TE prototype with HDH30 (PSSH content is 30%) film with a ΔT of 5 K over 72 h. Reproduced with permission. Copyright 2019 Wiley-VCH Verlag GmbH & Co. PET, (PEDOT)polyethylene terephthalate
FIGURE 9  (A) Wearable thermoelectric cooler (TEC) module for personalized cooling. The left schematic illustrating the thermal diffusion at the skin-TEC devices. Arrows display heat flow from human skin to the environment via TEC and heat sink. (B) Cold-side temperature of the wearable TEC versus fill factor (FF) at different aspect ratios (AR). Reproduced with permission under the terms of the CC-BY Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/). Copyright 2019, The Author, Springer Nature. (C) Photograph of flexible poly(Ni-ett) films on suspended parylene. Scale bar: 2 mm. (D) Time monitoring of the real-time temperature of the two contacts in an organic TEC device. Plots represent the $\Delta T$ of two contacts as a function of different current densities. The inset displays the infrared image of a TEC device with a current of 0.3 A/mm$^2$. (E) Simulated heat transport performance of poly(Ni-ett) based ultrathin device (the inset graph) and (F) Relative cooling capacity of poly(Ni-ett) film based cooler compared to Bi$_2$Te$_3$ based device. The performance is calculated with varied thickness and current densities. The excellent TE performance of OTE films enables its outstanding cooling properties along the vertical direction. Reproduced with permission under the terms of the CC-BY Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/). Copyright 2018, The Author, Springer Nature.
10 million cycles, and cooling stability exceeding 1 month. Kishore et al. \textsuperscript{32} investigated the combined effects of TEC design parameters, including the leg dimensions, fill factor (FF), and aspect ratio (Figure 9A,B). Combining experimental and thermotistical studies, high cooling performance can be achieved using: (1) a TE material with a high Seebeck coefficient to provide the higher cooling capacity; (2) a TE material with superior electrical conductivity, which can yield a higher coefficient of performance; and (3) TEC modules with low thermal resistance environment and high-FF (>20%) or high thermal resistance and low-FF (>20%). Based on these requirements, they demonstrated that the cooling efficiency of the ultra-low FF TEC based on-body cooler can be 170% higher than that of a commercial TEC with 500% fewer TE materials.\textsuperscript{32} These properties enable a wearable cooler to reduce the temperature of the human skin by 8.2 K. By fabricating thermally suspended devices combined with and interlocked infrared imaging technique, we overcome the limitation imposed by the inorganic Peltier effect (Figure 9C).\textsuperscript{109} In this study, a poly(Ni-ett) film was transferred to a suspended parylene substrate with patterned electrodes, in which the heat-insulation substrate contributes to the reduced thermal diffusion to the environment. Combing the measurements in a high vacuum level ($6 \times 10^{-4} \text{ Pa}$), a rectangular alternating current input, we separated the Peltier cooling effect and verified the Thomson relations in OTE materials. The real-time monitoring of the cooling temperature difference generated via applying current through the device (Figure 9D), yielding a maximum $\Delta T$ of 41 K based on the poly(Ni-ett) film. More interestingly, we estimated the heat transport capacity based on ultrathin poly(Ni-ett) films with optimized contacts and reasonable device geometry (Figure 9E,F).\textsuperscript{109} The performance of organic TEC is comparable with those of the commercial Bi$_2$Ti$_3$ modules, combined with the low thermal conductivity and high electric conductivity at room temperature, demonstrating a bright future of OTE materials in Peltier cooling in applications.

4 | CONCLUSION AND PERSPECTIVE

The aim of smart devices is not only to mimic biological behavior but also to perform automatic responses to complex stimuli, which raise critical requirements for functional materials. OTE materials have been developed rapidly over the past decade and will serve as key elements in different ISSs. However, OTE materials are still being developed with many unknown challenges. How can state-of-the-art OTE materials with ZT values greater than 0.5 be achieved for continued energy conversion? How can we overcome the bottleneck of stable doping? How can OTE devices function more intelligently, like biological organs? To answer these questions, tremendous effort should be devoted to designing new molecules, modulating mechanical properties, and endowing devices with multiple functionalities, all of which are key to satisfying smart applications.

Improving the performance and stability is at the heart of OTE materials. Despite previous investigations, only a few OTE materials have exhibited ZT values exceeding 0.1 and their operating stability is far from satisfactory. To improve TE performance significantly, both backbone and side-chain engineering must be emphasized to develop new materials. In particular, ordered molecular assemblies should be investigated further because the nanostructure of aggregates is crucial for determining phonon scattering and lattice thermal conductivity. For example, an organic superlattice structure as well as topological insulators are ideal for the electron-crystal phonon-glass model and enable an efficient TE conversion.\textsuperscript{310} However, its construction remains challenging owing to its complicated assembly process. In terms of stability, the fundamental mechanism of the de-doping process, such as the energy level mismatch and molecular distribution of host materials and dopants, has not been investigated systematically. Moreover, the temperature-dependent performance of the OTE materials, including the intrinsic carrier transport physics and de-doping property, also need to be considered to enable their application in long-time wearable and smart devices.

Looking beyond TE performance, the mechanical properties of OTE materials have to be optimized before they can be utilized in wearable electronics. Organic and hybrid materials are intrinsically flexible, and several TE textiles that convert thermal energy into electricity have been demonstrated. However, the operating repeatability and stability of flexible devices have rarely been investigated, particularly in regard to washability. Moreover, stretchability, another key mechanical property for wearable devices, has not been well resolved in OTE materials. To fulfill the elastic requirement, novel materials should be developed to achieve high TE performance at a stretch ratio of 50%,\textsuperscript{111,112} which is similar to that of human skin.

A more challenging task is the multifunctional integration of OTE devices. At first, an OTE device can be utilized as a self-powered sensor. Based on our previous proposal of an e-skin with a self-powered pressure/temperature sensor, better OTE devices can be developed such that they can respond to multiple stimuli. Second,
the development of OTE materials that can mimic biosystems is important. Considering the TE conversion mechanism in many biological behaviors, the ionic OTE materials and devices may be employed in bionic applications for better biocompatibility and sensitive signal transition. As an example, a glycoprotein-based gel from the electrosensors of sharks has been used in biological systems for dynamic temperature tracking. Third, further studies should be performed such that OTE devices are well integrated with other sensors and communication elements to enable a novel category of ISSs. Moreover, bioinspired functionalities such as self-protection and self-adaptation can be introduced into OTE devices to develop fascinating electronic applications.

As a new area in its infancy stage, many more issues exist and limit the realistic applications. For example, the biocompatibility and toxicity of OTE materials should be evaluated before they can be utilized in wearable elements. To date, these properties have not been considered. Moreover, the large-area and highly integrated fabrication of OTE devices with ultra-low-cost is not optimal yet. The roll-to-roll printing technique is effective for solving this issue; however, it is difficult to achieve using existing OTE and electrode materials. A solution to this is to develop an OTE ink based on a nonhalogenated solvent.

We conclude that OTE materials can be used to provide green energy as well as enable various smart devices. Combined material and device studies that assess TE performance, stability, processability, and multifunctional integration should be conducted. By solving the abovementioned challenges, OTE materials will be indispensable in the future intelligent society.

ACKNOWLEDGEMENTS
This research was financially supported by the National Key Research and Development Program of China (2017YFA0204700 and 2018YFC0200700), the National Natural Science Foundation of China (21805285, 22021002, 21905276, 61971396), the Natural Science Foundation of Beijing (4202077), Beijing National Laboratory for Molecular Sciences (BNLMS201912), UCAS (Y954011XX2) and CAS (ZDBS-LY-SLH034).

CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests.

ORCID
Fengjiao Zhang https://orcid.org/0000-0001-5088-1780
Chong-an Di https://orcid.org/0000-0002-6183-1321

REFERENCES
1. Meijer GCM. Smart Sensor Systems. New York, NY, USA: Wiley; 2008.
2. Cherenack K, Zysset C, Kinkeldei T, Munzenrieder N, Troster G. Woven electronic fibers with sensing and display functions for smart textiles. Adv Mater. 2010;22:5178-5182.
3. Koo JH, Kim DC, Shim HJ, Kim T-H, Kim D-H. Flexible and stretchable smart display: materials, fabrication, device design, and system integration. Adv Funct Mater. 2018;28:1801834.
4. Snyder GJ, Toberer ES. Complex thermoelectric materials. Nat Mater. 2008;7:105.
5. Rowe DM. Thermoelectrics Handbook: Macro to Nano. Boca Raton, FL, USA: CRC Press; 2006.
6. DiSalvo FJ. Thermoelectric cooling and power generation. Science. 1999;285:703.
7. Seebeck TJ. Magnetic polarization of metals and ores by temperature differences. German: Georg Reimer; 1821.
8. Sun T, Zhou B, Zheng Q, et al. Stretchable fabric generates electric power from woven thermoelectric fibers. Nat Commun. 2020;11:572.
9. Du Y, Cai K, Chen S, et al. Thermoelectric fabrics: toward power generating clothing. Sci Rep. 2015;5:6411.
10. Shi XL, Zou J, Chen ZG. Advanced thermoelectric design: from materials and structures to devices. Chem Rev. 2020;120:7399-7515.
11. Cai X, Sushkov AB, Suess RJ, et al. Sensitive room-temperature terahertz detection via the photothermoelectric effect in graphene. Nat Nanotechnol. 2014;9:814-819.
12. Suzuki D, Oda S, Kawano Y. A flexible and wearable terahertz scanner. Nat Photonics. 2016;10:809-813.
13. Kim SJ, We JH, Cho BJ. A wearable thermoelectric generator fabricated on a glass fabric. Energy Environ Sci. 2014;7:1959.
14. Zhang Q, Sun Y, Xu W, Zhu DB. Organic thermoelectric materials: emerging green energy materials converting heat to electricity directly and efficiently. Adv Mater. 2014;26:6829-6851.
15. Di CA, Xu W, Zhu DB. Organic thermoelectrics for green energy. Nat Sci Rev. 2016;3:269.
16. Russ B, Glaudell A, Urban JJ, Chabinyc ML, Segalman RA. Organic thermoelectric materials for energy harvesting and temperature control. Nat Rev Mater. 2016;1:16050.
17. Wu J, Sun Y, Xu W, Zhang Q. Investigating thermoelectric properties of doped polyaniline nanowires. Synth Met. 2014;189:177-182.
18. Sun YM, Di CA, Xu W, Zhu DB. Advances in n-type organic thermoelectric materials and devices. Adv Electron Mater. 2019;5:1800825.
19. Sun YH, Qiu L, Tang LP, et al. Flexible n-type high-performance thermoelectric thin films of poly(nickel-ethylenetetrathiolate) prepared by an electrochemical method. Adv Mater. 2016;28:3351-3358.
20. Liu J, van der Zee B, Alessandri R, et al. N-type organic thermoelectrics: demonstration of ZT > 0.3. Nat Commun. 2020;11:5694.
21. Kim G-H, Shao L, Zhang K, Pipe KP. Engineered doping of organic semiconductors for enhanced thermoelectric efficiency. Nat Mater. 2013;12:719-723.
22. Ding JM, Liu ZT, Zhao WR, et al. Selenium-substituted diketopyrrolopyrrole polymer for high-performance p-type organic thermoelectric materials. Angew Chem Int Ed. 2019;58:18994-18999.

23. Zhang FJ, Zang YP, Huang DZ, Di CA, Zhu DB. Flexible and self-powered temperature-pressure dual-parameter sensors using microstructure-frame-supported organic thermoelectric materials. Nat Commun. 2015;6:8356.

24. Zhao WR, Ding JM, Zou Y, Di CA, Zhu DB. Chemical doping of organic semiconductors for thermoelectric applications. Chem Soc Rev. 2020;49:7210-7228.

25. Lu Y, Wang J-Y, Pei J. Strategies to enhance the conductivity of n-type polymer thermoelectric materials. Chem Mater. 2019;31:6412-6423.

26. Beretta D, Perego A, Lanzani G, Caironi M. Organic flexible thermoelectric generators: from modeling, a roadmap towards applications. Sustain Energy Fuels. 2017;1:174-190.

27. Wang Y, Yang L, Shi XL, et al. Flexible thermoelectric materials and generators: challenges and innovations. Adv Mater. 2019;31:1807916.

28. Yao CJ, Zhang HL, Zhang Q. Recent progress in thermoelectric materials based on conjugated polymers. Polymers. 2019;11:107.

29. Wang M, Bi C, Li L, et al. Thermoelectric Seebeck effect in oxide-based resistive switching memory. Nat Commun. 2014;5:4598.

30. Pernstich KP, Rossner B, Batlogg B. Field-effect-modulated Seebeck coefficient in organic semiconductors. Nat Mater. 2008;7:321-325.

31. Johnson VA, Lark-Horovitz K. Theory of thermoelectric power in semiconductors with applications to germanium. Phys Rev. 1953;92:226-232.

32. Kishore RA, Nozariiahsmarz A, Poudel B, Sanghadasa M, Priya S. Ultra-high performance wearable thermoelectric coolers with less materials. Nat Commun. 2019;10:1765.

33. Ding J, Zhao W, Jin W, Di CA, Zhu DB. Advanced thermoelectric materials for flexible cooling application. Adv Funct Mater. 2021;31:2010695.

34. Gurevich YG, Logvinov GN. Physics of thermoelectric cooling. Semicond Sci Technol. 2005;20:R57-R64.

35. Anatyuchik LI, Luste OJ. Generalized thermoelectric Thomson relations. In Proceedings ICT’03. 22nd International Conference on Thermoelectrics (IEEE Cat. No.03TH8276), 2003; pp 491-492.

36. Pei J, Cai B, Zhuang H-L, Li J-F. Bi$_2$Te$_3$-based applied thermoelectric materials: research advances and new challenges. Natl Sci Rev. 2020;7:1856.

37. Gueye MN, Carella A, Faure-Vincent J, Demadrille R, Simonato J-P. Progress in understanding structure and transport properties of PEDOT-based materials: a critical review. Prog Mater Sci. 2020;108:100616.

38. Yue R, Xu J. Poly(3,4-ethylenedioxythiophene) as promising organic thermoelectric materials: a mini-review. Synth Met. 2012;162:912-917.

39. Bubnova O, Khan ZU, Malti A, et al. Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxythiophene). Nat Mater. 2011;10:429-433.

40. Sun YM, Sheng P, Di CA, et al. Organic thermoelectric materials and devices based on p- and n-type poly(metal 1,1,2,2-ethenetetrahaloate). Adv Mater. 2012;24:932-927.

41. Zhang FJ, Di CA. Exploring thermoelectric materials from high mobility organic semiconductors. Chem Mater. 2020;32:2688-2702.

42. Yan X, Xiong M, Li JT, et al. Pyrazine-flanked diketopyrrolopyrrole (DPP): a new polymer building block for high-performance n-type organic thermoelectrics. J Am Chem Soc. 2019;141:20215-20221.

43. Huang DZ, Yao HY, Cui YT, et al. Conjugated-backbone effect of organic small molecules for n-type thermoelectric materials with ZT over 0.2. J Am Chem Soc. 2017;139:13013-13023.

44. Huang DZ, Wang C, Zou Y, et al. Bismuth interfacial doping of organic small molecules for high performance n-type thermoelectric materials. Angew Chem Int Ed. 2016;55:10672-10675.

45. Chen R, Xu X, Yu D, et al. Highly stretchable and fatigue resistant hydrogels with low Young’s modulus as transparent and flexible strain sensors. J Mater Chem C. 2018;6:11193-11201.

46. Delalleau A, Josse G, Lagarde JM, Zahouani H, Berghen ME. A nonlinear elastic behavior to identify the mechanical parameters of human skin in vivo. Skin Res Technol. 2008;14:152-164.

47. Amjadi M, Yoon YJ, Park I. Ultra-stretchable and skin-mountable strain sensors using carbon nanotubes-Ecoflex nanocomposites. Nanotechnology. 2015;26:375501.

48. Mao L, Meng Q, Ahmad A, Wei Z. Mechanical analyses and structural design requirements for flexible energy storage devices. Adv Energy Mater. 2017;7:1700535.

49. Nan K, Kang SD, Li K, et al. Compliant and stretchable thermoelectric coils for energy harvesting in miniature flexible devices. Sci Adv. 2018;4:eaau5849.

50. Zheng Y, Ashizawa M, Zhang S, et al. Tuning the mechanical properties of a polymer semiconductor by modulating hydrogen bonding interactions. Chem Mater. 2020;32:5700-5714.

51. Döbler D, Kang J, Cooper CB, et al. Tuning the self-healing response of poly(dimethylsiloxane)-based elastomers. ACS Appl Polym Mater. 2020;2:4127-4139.

52. Cooper CB, Kang J, Yin Y, et al. Multivalent assembly of flexible polymer chains into supramolecular nanofibers. J Am Chem Soc. 2020;142:16814-16824.

53. Kiefer D, Yu L, Fransson E, et al. A solution-doped polymer semiconductor: insulator blend for thermoelectrics. Adv Sci. 2017;4:1600203.

54. Jeong YJ, Jung J, Suh EH, et al. Self-healable and stretchable organic thermoelectric materials: electrically percolated polymer nanowires embedded in thermoplastic elastomer matrix. Adv Funct Mater. 2019;30:1905809.

55. Wu J, Sun Y, Pei W-B, et al. Polyppyrrole nanotube film for flexible thermoelectric application. Synth Met. 2014;196:173-177.

56. Wei Q, Mukaida M, Kirihara K, Naitoh Y, Ishida T. Polymer thermoelectric modules screen-printed on paper. RSC Adv. 2014;4:28802-28806.
57. Liu LY, Sun YH, Li WB, et al. Flexible unipolar thermoelectric devices based on patterned poly[K,(Ni-ethylenetetrathiolate)] thin films. *Mater Chem Front*. 2017;1:2111-2116.

58. Luo T, Pan K. Flexible thermoelectric device based on poly (ether-b-amide12) and high-purity carbon nanotubes mixed bilayer heterogeneous films. *ACS Appl Energy Mater*. 2018;1:1904-1912.

59. Ferhat S, Domain C, Vidal J, et al. Organic thermoelectric devices based on a stable n-type nanocomposite printed on paper. *Sustain Energy Fuels*. 2018;2:199-208.

60. Diao Y, Shaw L, Bao Z, Mannsfeld SCB. Morphology control strategies for solution-processed organic semiconductor thin films. *Energy Environ Sci*. 2014;7:2145-2159.

61. Kim N, Lienemann S, Petsagkourakis I, et al. Elastic conduction polymer composites in thermoelectric modules. *Nat Commun*. 2020;11:1424.

62. Zhao D, Martinelli A, Willfahrt A, et al. Polymer gels with tunable ionic Seebeck coefficient for ultra-sensitive printed thermopiles. *Nat Commun*. 2019;10:1093.

63. Li P, Shang Z, Cui K, et al. Coaxial electrospinning core-shell fibers for self-healing scratch on coatings. *Chin Chem Lett*. 2019;30:157-159.

64. Hong SY, Oh JH, Park H, et al. Polyurethane foam coated with a multi-walled carbon nanotube/polyaniline nanocomposite for a skin-like stretchable array of multifunctional sensors. *NPJ Asia Mater*. 2017;9:e448-e448.

65. Ren W, Sun Y, Zhao D, et al. High-performance wearable thermoelectric generator with self-healing, recycling, and Lego-like reconfiguring capabilities. *Sci Adv*. 2021;7:eabe0586.

66. Liu K, Tran H, Feig VR, Bao Z. Biodegradable and stretchable polymeric materials for transient electronic devices. *MRS Bull*. 2020;45:96-102.

67. Khatib M, Zohar O, Haick H. Self-healing soft sensors: from material design to implementation. *Adv Mater*. 2021;33:2004190.

68. Sheng P, Sun YM, Jiao F, et al. A novel cuprous ethylenetetrathiolate coordination polymer: structure characterization, thermoelectric property optimization and a bulk thermogenerator demonstration. *Synth Met*. 2014;193:1-7.

69. Sondergaard RR, Hösel M, Espinosa N, Jørgensen M, Krebs FC. Practical evaluation of organic polymer thermoelectrics by large-area R2R processing on flexible substrates. *Energy Sci Eng*. 2013;1:81-88.

70. Ito M, Koizumi T, Kojima H, Saito T, Nakamura M. From materials to device design of a thermoelectric fabric for wearable energy harvesters. *J Mater Chem A*. 2017;5:12068-12072.

71. Wu Q, Hu J. A novel design for a wearable thermoelectric generator based on 3D fabric structure. *Smart Mater Struct*. 2017;26:045037.

72. Ryan JD, Lund A, Hofmann AI, et al. All-organic textile thermoelectrics with carbon-nanotube-coated n-type yarns. *ACS Appl Energy Mater*. 2018;1:2934-2941.

73. Liu LY, Sun YH, Li WB, et al. Flexible unipolar thermoelectric materials and power generators. *J Mater Chem A*. 2015;3:21428-21433.

74. Jo S, Choo S, Kim F, Heo SH, Son JS. Ink processing for thermoelectric materials and power-generating devices. *Adv Mater*. 2019;31:1804930.

75. Kim N, Lienemann S, Petsagkourakis I, et al. Elastomer conductive polymer composites in thermoelectric modules. *Nat Commun*. 2020;11:1424.

76. Zhao D, Martinelli A, Willfahrt A, et al. Polymer gels with tunable ionic Seebeck coefficient for ultra-sensitive printed thermopiles. *Nat Commun*. 2019;10:1093.

77. Li P, Shang Z, Cui K, et al. Coaxial electrospinning core-shell fibers for self-healing scratch on coatings. *Chin Chem Lett*. 2019;30:157-159.

78. Hong SY, Oh JH, Park H, et al. Polyurethane foam coated with a multi-walled carbon nanotube/polyaniline nanocomposite for a skin-like stretchable array of multifunctional sensors. *NPJ Asia Mater*. 2017;9:e448-e448.

79. Ren W, Sun Y, Zhao D, et al. High-performance wearable thermoelectric generator with self-healing, recycling, and Lego-like reconfiguring capabilities. *Sci Adv*. 2021;7:eabe0586.

80. Kee S, Haque MA, Corzo D, Alshareef HN, Baran D. Self-healing and stretchable 3D-printed organic thermoelectrics. *Adv Funct Mater*. 2019;29:1905426.

81. Dai X, Zhang Y, Gao L, et al. A mechanically strong, highly stable, thermoplastic, and self-healable supramolecular polymer hydrogel. *Adv Mater*. 2015;27:3566-3571.

82. Liu K, Tran H, Feig VR, Bao Z. Biodegradable and stretchable polymeric materials for transient electronic devices. *MRS Bull*. 2020;45:96-102.

83. Khatib M, Zohar O, Haick H. Self-healing soft sensors: from material design to implementation. *Adv Mater*. 2021;33:2004190.

84. Sheng P, Sun YM, Jiao F, et al. A novel cuprous ethylenetetrathiolate coordination polymer: structure characterization, thermoelectric property optimization and a bulk thermogenerator demonstration. *Synth Met*. 2014;193:1-7.

85. Sondergaard RR, Hösel M, Espinosa N, Jørgensen M, Krebs FC. Practical evaluation of organic polymer thermoelectrics by large-area R2R processing on flexible substrates. *Energy Sci Eng*. 2013;1:81-88.
enabling NIR detection. *ACS Appl Mater Interfaces*. 2015;7:8968-8973.

94. Guo W, Dong Z, Xu Y, et al. Sensitive terahertz detection and imaging driven by the photothermoelectric effect in ultrathin-channel black phosphorus devices. *Adv Sci*. 2020;7:1902699.

95. Luxmoore JI, Liu PQ, Li P, Faist J, Nash GR. Graphene-metamaterial photodetectors for integrated infrared sensing. *ACS Photonics*. 2016;3:936-941.

96. Li Y, Zhang Y, Li T, et al. A fast response, self-powered and room temperature near infrared-terahertz photodetector based on a MAPbI3/PEDOT:PSS composite. *J Mater Chem C*. 2020;8:12148-12154.

97. Zhao WR, Zhang FJ, Dai XJ, et al. Enhanced thermoelectric performance of n-type organic semiconductor via electric field modulated photo-thermoelectric effect. *Adv Mater*. 2020;32:2000273.

98. Yang Y, Lin Z-H, Hou T, Zhang F, Wang ZL. Nanowire-composite based flexible thermoelectric nanogenerators and self-powered temperature sensors. *Nano Res*. 2012;5:888-895.

99. Jung M, Jeon S, Bae J. Scalable and facile synthesis of stretchable thermoelectric fabric for wearable self-powered temperature sensors. *RSC Adv*. 2018;8:39992-39999.

100. Wang YF, Sekine T, Takeda Y, et al. Fully printed PEDOT:PSS-based temperature sensor with high humidity stability for wireless healthcare monitoring. *Sci Rep*. 2020;10:2467.

101. Jung M, Kim K, Kim B, et al. Paper-based bimodal sensor for electronic skin applications. *ACS Appl Mater Interfaces*. 2017;9:26974-26982.

102. Ding T, Chan KH, Zhou Y, et al. Scalable thermoelectric fibers for multifunctional textile-electronics. *Nat Commun*. 2020;11:6006.

103. Han S, Jiao F, Khan ZU, et al. Thermoelectric polymer aerogels for pressure-temperature sensing applications. *Adv Funct Mater*. 2017;27:1703549.

104. Kim B, Na J, Lim H, et al. Robust high thermoelectric harvesting under a self-humidifying bilayer of metal organic framework and hydrogel layer. *Adv Funct Mater*. 2019;29:1807549.

105. Cui L, Miao R, Wang K, et al. Peltier cooling in molecular junctions. *Nat Nanotechnol*. 2018;13:122-127.

106. Zhao D, Tan G. A review of thermoelectric cooling: materials, modeling and applications. *Appl Therm Eng*. 2014;66:15-24.

107. Li G, Garcia Fernandez J, Lara Ramos DA, et al. Integrated microthermoelectric coolers with rapid response time and high device reliability. *Nat Electron*. 2018;1:555-561.

108. Chowdhury I, Prasher R, Lofgreen K, et al. On-chip cooling by superlattice-based thin-film thermoelectrics. *Nat Nanotechnol*. 2009;4:235-238.

109. Jin WL, Liu LY, Yang T, et al. Exploring Peltier effect in organic thermoelectric films. *Nat Commun*. 2018;9:3586.

110. Zhi DF, Di CA, Zhu DB. Organic topological insulators (OTI): a dream coming true.? *Nat Sci Rev*. 2020;7:996-997.

111. Yamada T, Hayamizu Y, Yamamoto Y, et al. A stretchable carbon nanotube strain sensor for human-motion detection. *Nat Nanotechnol*. 2011;6:296-301.

112. Hu W, Zhang H, Salaika K, Sirringhaus H. *SmartMat*: Smart materials to Smart world. *SmartMat*. 2020;1:e1014.

113. Brown BR. Sensing temperature without ion channels. *Nature*. 2003;421:495.

### AUTHOR BIOGRAPHIES

**Vue Zhao** received his BS degree in nano material and technology from Beijing Jiaotong University (2020). Since 2020, he has been at the Key Laboratory of Organic Solids in ICCAS for a Ph.D. degree. His current research interest is on organic thermoelectric materials and devices.

**Liyao Liu** received her Ph.D. degree from Institute of Chemistry, Chinese Academy of Sciences (ICCAS) in 2019, and joined the ICCAS as a technician. Her research interests are focused on organic thermoelectric materials and devices.

**Fengjiao Zhang** received her Ph.D. degree from Institute of Chemistry, Chinese Academy of Sciences (ICCAS) in 2015, and joined the University of CAS in 2019 after the postdoctoral research in University of Illinois at Urbana-Champaign. Her research interests include the fabrication, performance optimization and application development of organic bioelectronic devices.

**Chong-an Di** is a professor of Organic Solids Laboratory in the ICCAS. He finished his Ph.D. study in Chemistry from ICCAS, in 2008, and was appointed as a professor in 2016 at ICCAS. Currently, his research focuses on the investigation of the organic thin-film transistors and organic thermoelectrics.

**Daoben Zhu** is a professor and director of the Organic Solids Laboratory in the Institute of Chemistry, CAS. He finished his graduate courses at the East China University of Science and Technology in 1968. He was selected as an academician of the CAS in 1997. His research interests include molecular materials and devices.

---

**How to cite this article:** Zhao Y, Liu L, Zhang F, Di C-a, Zhu D. Advances in organic thermoelectric materials and devices for smart applications. *SmartMat*. 2021;1-20. https://doi.org/10.1002/smm2.1034