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Thermally drawn flexible inorganic thermoelectric fibers

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Thermoelectric materials can directly realize the mutual conversion of heat and electric energy. Thermoelectric generation and refrigeration devices have advantages such as environmental friendliness, low energy consumption and small size, making them an effective means of achieving carbon neutrality [1]. More importantly, with the rapid development of wearable electronic products, the demand for portable and wearable energy supply devices has significantly increased. Furthermore, the frequent occurrence of extreme weather has prompted people to rely more on-air conditioning, which aggravates the energy crisis and necessitates zero-carbon personal thermal management technology. Hence, flexible thermoelectric fibers will play an important role in addressing these challenges by enabling the weaving of wearable thermoelectric fabrics for body-heat sensing, power generation and thermoregulation [2]. Flexible thermoelectric fibers can effectively contact and cover heat sources with curved surfaces, thereby maximizing the heat absorption rate and thermoelectric conversion efficiency. They can adapt to complex deformations, such as various twists and stretches, enabling the woven thermoelectric fabric to have unique properties such as breathability and moisture-wicking.

Nowadays, flexible fibers based on organic thermoelectric materials exhibit poor thermoelectric performance, while flexible fibers based on inorganic thermoelectric materials deposited on the surface of traditional yarns have disadvantages such as susceptibility to delamination, complex manufacturing processes, and high costs. The major challenge lies in economically incorporating high-performance inorganic thermoelectric materials directly into flexible fibers on a large scale. Herein, a novel preform-to-fiber technology based on the thermal drawing method is introduced, which fabricates inorganic thermoelectric fibers with fiber-optic length scales, flexibility, and uniformity. As shown in Figure 1, the crystal structure of flexible inorganic thermoelectric fibers can be controllably regulated to be amorphous, polycrystalline, or single crystalline according to the application requirements. These fibers can also be woven into wearable thermoelectric fabrics to monitor and regulate body temperature while generating electricity. Moreover, it is anticipated that future flexible thermoelectric fibers with good mechanical properties will be based on plastic inorganic semiconductors.

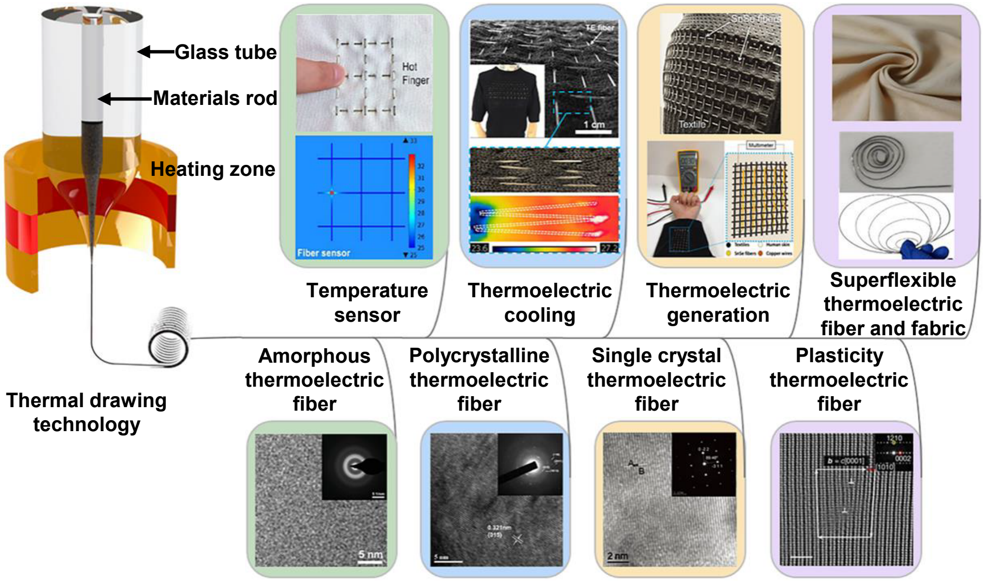

Figure 1 The schematics of flexible thermoelectric fibers including thermally drawn fiber technology, crystal structures of fiber cores (amorphous thermoelectric fiber, polycrystalline thermoelectric fiber, single crystal thermoelectric fiber and plasticity thermoelectric fiber), and wearable fabric applications (temperature sensor, thermoelectric cooling, thermoelectric generation and superflexible thermoelectric fabric). The map element in the figure was modified with permission from Refs. [3–5].

Thermal drawing method for flexible inorganic thermoelectric fibers. Commonly, the methods for preparing thermoelectric fibers include dry fabrication methods, solution-based processes, and spinning processes [6]. However, dry fabrication methods, such as physical vapor deposition and chemical vapor deposition, require vacuum and high-temperature conditions. Solution-based methods (such as dip coating and printing), and spinning processes (such as electrospinning and wet-spinning) are limited by difficulties in large-scale manufacturing and a lack of potential for designing complex structures. In contrast, the thermal drawing method offers unique advantages, including customizable structures, large-scale manufacturing capabilities, and easy integration with other processes. Additionally, this method enables the integration of various functional materials into a fiber, which provides the possibility for the efficient fabrication of flexible fiber-shaped electronic devices. Briefly, the process begins with the macroscopic preparation of a preform that comprises core inorganic thermoelectric materials and cladding glass or polymer, which is then vacuum-sealed with a designed device structure. The preform is heated in the furnace of a drawing tower and then scaled down to microscopic dimensions through thermal drawing, resulting in a fiber that retains the same device structure as the preform. The cladding material is selected based on its glass transition temperature, which must be slightly higher than the melting point of the core inorganic thermoelectric materials. This ensures that the viscosity of the glass cladding is sufficient to provide structural support to the liquid thermoelectric cores, allowing for the production of hundreds of meters of continuous fibers. The fiber diameter and tension are controlled by the heating temperature of the furnace, the feeding speed of the preform, and the drawing speed of the fiber. During the high-temperature drawing process, it is crucial to avoid chemical reactions and mismatches in thermal expansion coefficients between the thermoelectric materials and cladding materials, as these could cause fiber fractures due to internal stress. Since thermoelectric fibers produced through the thermal drawing method generally undergo rapid air cooling, they tend to form an amorphous or polycrystalline structure. High-quality single-crystal or polycrystalline fibers can be obtained through subsequent annealing or laser zone melting recrystallization technology for performance optimization.

Amorphous thermoelectric fiber. Amorphous thermoelectric fibers prepared using the thermal drawing method exhibit good flexibility and greatly enhance the comfort of wearable fiber devices. Furthermore, amorphous thermoelectric materials possess a high Seebeck coefficient, making them suitable for temperature sensors. To meet the growing demand for flexible, large-area, low-cost, and high-spatiotemporal resolution thermal sensing networks in industrial processing, medical diagnosis, and military defense, Zhang *et al*. [3] thermally drew macroscopic preform rods containing amorphous thermoelectric glass cores and polymer cladding into flexible fibers with thermal sensing functions. The thermoelectric fiber sensor can operate over a wide temperature range with high thermal detection sensitivity and accuracy. Moreover, a single thermoelectric fiber can detect point temperature changes and locate cold/heat points along the fiber. A two-dimensional fiber array can determinate temperature distribution and pinpoint cold/heat source locations with millimeter-scale spatial resolution, demonstrating applications in thermometry, smart sensors, e-skin for robotics, and wearable electronics.

Polycrystalline thermoelectric fiber. Bismuth telluride-based thermoelectric materials, which have a narrow band gap and excellent thermoelectric properties at room temperature, are currently the most widely used polycrystalline thermoelectric materials in industrial production [6]. Zhang *et al*. [4] demonstrated the fabrication of flexible and ultra-long thermoelectric fibers using the thermal drawing method, which seamlessly integrates high-performance, intrinsically crystalline inorganic thermoelectric micro/nanowires into fibrous carriers. The thermoelectric properties of P-type $Bi_{0.5}Sb_{1.5}Te_3$ and N-type Bi_2Se_3 polycrystalline fibers were tested. The results showed that these fibers maintain the same high thermoelectric properties as their inorganic bulk counterparts. Moreover, the thermoelectric fibers were used to construct two types of thermoelectric generators that can cover different surfaces, and the thermoelectric fibers were further woven into two-dimensional textiles to achieve temperature regulation. These results suggest that these fibers can be integrated into fabrics to build wearable thermoelectric devices, and also effectively connect hot and cold sources on different curved surfaces, overcoming the limitations of traditional bulk thermoelectric devices.

Single crystal thermoelectric fiber. Single crystal thermoelectric material SnSe is reported to have the highest performance among thermoelectric materials [7]. However, the rigid and bulky nature of SnSe makes it unsuitable for flexible and wearable device applications [8]. Zhang *et al*. [5] demonstrated a method called laser-induced directional crystallization to fabricate ultra-long single crystal SnSe fibers with a rock salt structure and high thermoelectric properties, with diameters ranging from the micro to nanometer scale. This method overcomes the challenges of preparing high-quality single crystal flexible thermoelectric fibers and enables the large-scale growth of single crystal fiber materials. Directional recrystallization of the fibers is achieved by establishing a stable and confined melt zone across the entire fiber. As the narrow molten region translates with the laser scanning, the polycrystalline material melts at the forward edge and leaves behind a single crystalline material. Both theoretical and experimental studies show that SnSe fibers possess high thermoelectric properties, with the ZT value increasing to 2 at 862 K. This method offers a promising avenue for utilizing fiber-shaped single crystal materials in applications ranging from one-dimensional fiber devices to multi-dimensional wearable fabrics.

Conclusion and perspective. Inorganic thermoelectric fibers based on the thermal drawing method have emerged as an effective approach for developing flexible thermoelectric devices. Although these inorganic thermoelectric fibers exhibit excellent thermoelectric properties, their weak mechanical properties limit their application in the field of wearable thermoelectric fabrics, because industrial looms require fiber strength for weaving, and fabrics need fiber plasticity to prevent fractures during bending. With the recent emergence of plastic thermoelectric semiconductors, such as AgCu(Se,S,Te) [9] and Mg_3Bi_2 [10], future research on thermoelectric fibers should focus on: (1) employing plastic inorganic thermoelectric compounds and understanding their deformation mechanisms to improve both the thermoelectric and plastic properties of the fiber core; (2) replacing the fiber cladding with flexible polymer materials to improve the mechanical properties of the fiber; (3) eventually yielding flexible inorganic fibers with high thermoelectric properties and excellent mechanical properties including tensile strength and plastic strain to meet the requirements of weaving high-performance wearable thermoelectric fabrics.

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Author contributions

C.W. proposed the topic of the perspective, wrote the manuscript, and designed the figures. T.Z. and L.D.Z. edited, reviewed, discussed and revised the manuscript. All authors have given approval to the final version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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