Review Article

Advanced Thermally Drawn Multimaterial Fibers: Structure-Enabled Functionalities

Zhe Wang ¹, Mengxiao Chen ¹, Yu Zheng^{1,2}, Jing Zhang ³, Zhixun Wang¹, Jiao Yang¹, Qichong Zhang^{1,2}, Bing He¹, Miao Qi¹, Haozhe Zhang ¹, Kaiwei Li ⁴, and Lei Wei ^{1,2}

¹School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

²CINTRA CNRS/NTU/THALES, UMI3288, Research Techno Plaza, 50 Nanyang Drive, Singapore 637553

³School of Mechanical Engineering and Electronic Information, China University of Geosciences (Wuhan), Wuhan, China

⁴Institute of Photonics Technology, Jinan University, Guangzhou 511443, China

Correspondence should be addressed to Mengxiao Chen; chenmx@ntu.edu.sg and Lei Wei; wei.lei@ntu.edu.sg

Received 27 December 2020; Accepted 19 February 2021; Published 13 March 2021

Copyright © 2021 Zhe Wang et al. Exclusive Licensee Beijing Institute of Aerospace Control Devices. Distributed under a Creative Commons Attribution License (CC BY 4.0).

Thermally drawn multimaterial fibers have experienced rapid development in the past two decades owing to the high scalability, uniformity, and material and structure compatibility of the thermal drawing technique. This article reviews various multimaterial fibers based on different functional structures and their applications in disparate fields. We start from the functional structures achieved in optical fibers developed in the early stage of thermally drawn fibers. Subsequently, we introduce both typical functional structures and unique structures created in multimaterial fibers for varying applications. Next, we present the early attempts in breaking the axial symmetric structures of thermally drawn fibers for extended functionalities. Additionally, we summarize the current progress on creating surface structures on thermally drawn fibers. Finally, we provide an outlook for this trending topic towards wearable devices and smart textiles.

1. Introduction

Fabrics have served as an indispensable product in everyday life for thousands of years [1]. Although they were used in tremendous applications with various forms ranging from small pieces, including bandages and towels, to different kinds of apparel, the basic functions of these fabrics have not evolved much from ancient to modern times. In most cases, they are considered lacking technological functions and used in cleaning, offering physical protection from the external environment, achieving thermal comfort, or providing aesthetic expression. In the last few decades, the leaping semiconductor industry enabled the rapid development of electronic devices with numerous functions such as sensing, communicating, computing, and actuating. Moreover, these devices are getting smaller in size and lighter in weight, making them portable for ease of use and implementation. Inspired by these achievements, escalating research interests have focused on realizing different functions, such as vital sign monitoring, external environment detection, and data

transmission, on fabrics to construct wearable fabric-based devices [2].

Fibers, as the building blocks of fabrics, determine the basic properties and the realization of functionalities on fabrics. Thus, the scalable fabrication of flexible fibers compatible with various materials and complex architectures is highly demanded to support the development of functional fabrics and their wide range of applications. Unfortunately, it is quite challenging to employ fiber as a new platform to develop functional devices. Current processing techniques, such as lithography and molecular beam epitaxy, are mostly developed for rigid and planar substrates such as wafers, which are not compatible with the soft and highly curved fibers. Besides, the commonly used materials, such as silicon, and planar structure configuration in conventional devices are difficult to be transferred to fibers. Hence, countless works have been carried out to explore new processing techniques for fiber-based devices. Electrospinning [3], dip coating [4], chemical and physical deposition [5], electrochemical deposition [6], and hydrothermal synthesis [7] have been

FIGURE 1: Various functional structures achieved in thermally drawn fibers. Reproduced with permission. Copyright 2012, AAAS [96]. Reproduced under the terms of the Creative Commons Attribution-NonCommercial license (CC BY-NC 4.0). <https://creativecommons.org/licenses/by-nc/4.0/> [97]. Reproduced under the terms of the Creative Commons Attribution license (CC BY 4.0). <https://creativecommons.org/licenses/by/4.0/> [43, 64, 70, 77, 81, 98]. Reproduced with permission. Copyright 2006, Wiley-VCH [58]. Reproduced with permission. Copyright 2012, Wiley-VCH [28]. Reproduced with permission. Copyright 2018, National Academy of Sciences [65]. Reproduced with permission. Copyright 2014, Wiley-VCH [82]. Reproduced with permission. Copyright 2016, published by Springer Nature [74]. Reproduced with permission. Copyright 2016, Wiley-VCH [76]. Reproduced with permission. Copyright 2017, Wiley-VCH [83].

extensively studied as fiber processing methods. As a result, various fiber functionalities and promising fiber applications such as solar cells, supercapacitors, and light-emitting devices were demonstrated [8]. However, these approaches require complex material deposition procedures to form a single fiber. Moreover, structures of fibers fabricated by the techniques mentioned above are usually restricted to homogeneous or layered core-shell structures, leading to limited functionalities. Additionally, the weaknesses in durability, uniformity, and scalability in the production of these fibers also become the bottleneck towards industrial production.

Recently, a preform-to-fiber thermal drawing technique has been broadly employed for the mass production of longitudinally uniform fibers with an extended length up to tens of kilometers [9]. This thermal drawing technique was originally used to fabricate glass and polymer fibers for optical communication. Owing to their high production rate, axial uniformity, and stability, optical fibers have become an indispensable item implemented all over the world for long-distance light data transmission today. Further, microscopic fiber with elaborate inner structures could be achieved simply by constructing the corresponding structure in the macroscopic preform [10]. Therefore, to date, various sophisticated

structures have been achieved inside optical fibers, demonstrating many other applications such as fiber laser [11], imaging optics [12], and fiber-optic sensor [13, 14]. Encouraged by these achievements in optical fibers, researchers start to incorporate different functional materials such as metals and semiconductors in thermally drawn fibers. Because of the superior flexibility in fiber structure design, different materials could be arbitrarily assigned to form disparate functional structures. In the past two decades, these multimaterial fibers with varying functional structures have exhibited their tremendous potential in various research fields including optoelectronics [15, 16], electronics [17], micro/nanofabrication [18, 19], and neural interfaces [20]. In this review article, we will focus on functional structures achieved in thermally drawn fibers and discuss their potential applications, as shown in Figure 1. We will start from the structures in kinds of optical fibers, which is the original purpose of this thermal drawing technique. Then, we will introduce the various functional structures achieved in the newly developed multimaterial fibers. Subsequently, some efforts for breaking the axial symmetry of the thermally drawn fibers are discussed. Besides inner structures, we will also present the recent studies on creating micro/nanostructures on fiber surfaces at last.

FIGURE 2: Schematic of the thermal drawing process and optical fibers with different structures. (a) Schematic of the thermal drawing process. (b) Schematic of hollow-core Bragg fibers. (c) Schematic of hollow-core microstructured fiber with several rings of air holes separated by nanoscale support bridges. (d) Schematic of hollow-core PBG fiber. (e) Optical image of all solid PBG fibers. Reproduced with permission. Copyright 2007, The Optical Society [44]. (f) SEM image of antiresonant hollow-core optical fiber. Reproduced under the terms of the Creative Commons Attribution license (CC BY 4.0). <https://creativecommons.org/licenses/by/4.0/> [98]. (g) Functional material (ZnSe) deposited in hollow-core fiber via HPCVD. Reproduced with permission. Copyright 2011, Wiley-VCH [99].

2. Thermal Drawing Process

The thermal drawing process begins with preparing a macroscopic preform where glassy materials, such as silica and thermoplastic polymer, constitute a great portion of the structural materials. The material and architecture of the resulting thermally drawn fiber are consistent with those of the preform. Therefore, a well-constructed preform with the desired material located at the prescribed position is requisite to achieve various functional fibers. Till now, many preform preparation approaches have been developed to enable a wide range of functional fiber structures, such as rod-in-tube [21], extrusion [22], thin-film rolling [23], deep-hole drilling [24], casting [25], fused deposition modeling [26], double crucible [27], direct assembly [28], and additive manufacturing [29].

The schematic of the preform-to-fiber thermal drawing process is shown in Figure 2(a). The prepared preform is firstly fixed above a vertical tube furnace, and a weight may be attached below the preform. Then, the preform is fed down into the furnace and held in the place where the bottom part of the preform is below the heating zone of the furnace. The temperature is set according to the cladding material of the preform, usually 50–100°C higher than its glass transition temperature. After around half an hour, the temperature of the material at the heating zone is high enough to become soft and necked down under the pulling of the attached weight or the weight of the preform's bottom part. The size of the preform reduces in the neckdown region and finally forms a fiber. To draw the fiber continuously, the preform is then fed into the heating zone at a constant speed (v_p) while the fiber is drawn down and collected by a capstan at a much larger speed (v_f), as sketched in Figure 2(a). Since

the total volume of the materials remains unchanged during the thermal drawing process, the diameter of the fiber can be controlled by the preform speed and fiber speed, as the equation described below:

$$D_{\text{fiber}} = D_{\text{preform}} \times \sqrt{\frac{v_p}{v_f}}. \quad (1)$$

In this manner, a hundred-meter-long fiber with a diameter ranging from hundreds of micrometers to several millimeters can be drawn from a hundred-millimeter-long preform with a diameter of several centimeters, while the feature size of the fiber inner structure may reach as small as tens of nanometers.

To ensure that the resulting fiber possesses an identical structure as predesigned, several general criteria should be applied when selecting different materials for codrawing. Firstly, the preform must consist of at least one thermoplastic material to support the whole structure from collapse. In general, this thermoplastic material should possess a high viscosity (usually 10^4 – 10^8 Pa·s) under its drawing temperature to keep the complex structure from deformation. Secondly, all the other materials inside the preform should be softened or molten under the drawing temperature. And the boiling temperature of the crystalline materials should be higher than the drawing temperature. Thirdly, the materials in the preform should better have similar thermal expansion coefficients to prevent mechanical fractures during the rapid cooling down process after being drawn into fiber. Lastly, all the materials should be chemically stable without decomposition or interpenetration. Also, chemical reactions should be generally avoided to ensure a steady and continuous drawing

process. However, in some special cases, in-fiber chemical reactions during the thermal drawing process could be leveraged to fabricate fibers with extended materials and architecture selections [30, 31].

3. Functional Structures in Optical Fibers

Conventional optical fibers usually have a solid cylindrical core-cladding structure. The refractive index of the fiber core is slightly larger than the cladding to ensure that the light could be confined in the core and achieve total internal reflection at the interface between the fiber core and the cladding. This slight refractive index difference could be realized by doping rare earth elements. According to the refractive index distribution in the cross section, the conventional optical fibers could be divided into step-index fiber and graded-index fiber. Both step-index fiber and graded-index fiber can be further divided into single-mode fiber and multimode fiber depending on their structure size and refractive index distribution. As this simple all-solid structure optical fiber is easy to fabricate at a large scale and possesses ultralow transmission loss, the conventional optical fibers have been widely used in telecommunication [32], power transmission [33], fiber optic sensor [34], etc.

In the past few decades, microstructured optical fibers (MOFs) have attracted intensive research interests because of their capability of tunable inner structure, which enables MOF to have lots of unique optical properties that cannot be achieved in conventional optical fibers, such as high nonlinearity [35], tunable dispersion [36], and large mode area [37]. A large group of MOFs is the photonic bandgap (PBG) fibers. PBG fibers are a kind of optical fiber that comprises sophisticated microstructures to confine light by photonic bandgap effect instead of total internal reflection [38]. Bragg fibers are fabricated in the early stage of the development of hollow-core PBG fibers [39]. Such Bragg fibers usually consist of a hollow core and an alternating multilayered structure in the cladding area formed by two materials with a large difference in refractive index, such as polyethersulfone (PES) and As_2Se_3 [40], as demonstrated in Figure 2(b). As a photonic bandgap is formed by the periodic alternating layers, light with a specific frequency will be confined inside the hollow core and transmit along the fiber. Thus, this specific frequency is tunable by simply changing the thickness of each layer [41]. Also, this Bragg fiber possesses a low loss as the light is transmitted in air other than solid fiber materials. The reported loss of the PBG fiber with a fundamental bandgap at $10.6\ \mu\text{m}$ is $0.95\ \text{dB/m}$, which is much lower than that of the state-of-art photonic crystal fiber whose loss is $2.1\ \text{dB/m}$ [42]. Besides the hollow-core Bragg fibers constructed from an alternating multilayered structure, there are some other types of PBG fibers. As shown in Figure 2(c), instead of using materials with different refractive indexes to form a multilayered structure, the dielectric layers can also be formed by rings of air holes separated by nanoscale support bridges [43]. Such dielectric rings form the photonic bandgap to guide light in the hollow core, whose refractive index is smaller than that of the surrounding cladding material. Moreover, the photonic bandgap could also be formed from

a 2D periodical array of air holes in a dielectric material (Figure 2(d)), which has been widely studied as another type of PBG fibers since it was first demonstrated in 1998 [38]. Additionally, the PBG fiber with a 2D periodical array can also be formed without air holes but with high-index rods in the low-index background, as shown in an all-solid PBG fiber in Figure 2(e) [44]. The fundamentally different light guidance mechanism from total internal reflection enables PBG fibers to have numerous intriguing optical properties, such as ultralow optical nonlinearity, low latency, and high damage threshold [45]. These advantages enable the PBG fibers to have a series of applications such as cylindrical optical resonators [46], high-power laser transmission [40], surface-emitting fiber lasers [11], gas sensing [47], and particle guidance [48].

Another type of MOFs is antiresonant hollow-core optical fiber, as shown in Figure 2(f). The cladding layer of this fiber forms a Fabry-Perot (F-P) cavity. This cavity could be considered transparent when the light is in resonance with the cavity, and thus, the light will leak through the cladding, while there will be a high reflection in the cavity when the antiresonance occurs, confining the light in the fiber core. Recently, the loss of this antiresonant hollow-core optical fiber has been reported to be reduced to $0.28\ \text{dB/km}$ at the wavelength ranging from 1510 to 1600 nm [49]. Moreover, owing to its simple waveguiding mechanism, antiresonant hollow-core optical fibers possess many other advantages over hollow-core PBG fibers, such as high laser damage threshold and broadband light propagation, predicting their promising applications including mid-infrared fiber gas laser [50], chirped pulse amplifier [51], and biochemical sensing [52].

Additionally, MOFs can also be used as templates for depositing functional materials inside their air channels via the high-pressure chemical vapor deposition (HPCVD) process. This process utilizes precursors mixed with carrier gases flowing through the air channel inside a fiber. And the high temperature at the required location induces the decomposition of the precursors and depositing the desired material on the wall of the air channel. As the surfaces of the thermally drawn fiber are extremely smooth [53] and the inner diameter of the air channel is small enough (10^{-8} to $10^{-4}\ \text{m}$) to sustain a high pressure in MPa level, the desired material can be deposited at high speed with a low scattering interface on the channel wall. As shown in the cross-sectional image in Figure 2(g), many functional materials including platinum (Pt), zinc selenide (ZnSe), and silicon (Si) have been deposited inside fibers via the HPCVD process for various applications in photodetection, fiber amplifiers, optical communications, etc. [18]

4. Functional Structures in Multimaterial Fibers

Inspired by these various fiber structures and applications achieved in optical fibers and the intriguing capabilities of thermal drawing, escalating research interests have been focused on integrating more functional materials into fibers with predesigned structures to explore the potential applications of multimaterial fibers in optoelectronics, electronics,

microfluidics, etc. [54]. As high flexibility is always an important performance for fiber-based devices, the multimaterial fibers are mostly based on thermoplastic polymers. Owing to the low process processing temperature and good processing performance of polymers, more complex and irregular structures could be realized in the polymer preform for extensive applications.

The ability to incorporate conductors and semiconductors enables multimaterial fibers to have disparate functionalities. A typical structure for such multimaterial fibers is shown in Figure 3(a) [55]. A semiconducting $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ (GGT) glass is employed as the fiber core between two $\text{Zn}_{10}\text{Sn}_{90}$ electrodes. And this whole structure is encapsulated in polysulfone (PSU) polymer cladding, which serves as the supporting material during the thermal drawing process and the protective layer of the fiber. The GGT glass is a phase-change material that can change its phase between amorphous and crystalline upon heated electrically or optically. Therefore, this fiber can be used as an ovonic memory switching device. As shown in Figure 3(b), the as-drawn GGT core is in an amorphous state, which has a large resistance (“OFF” state). When a voltage is applied to the electrodes and increased to 150 V, the GGT core is crystallized after being heated electrically, and the resistance drops significantly, indicating an “ON” state. This switching voltage can be greatly reduced when the fiber is heated on a hot plate. Besides this ovonic memory switching, many other functionalities have been demonstrated using similar structures, such as photodetection [56, 57] and thermal sensing [58].

In some applications such as photodetector and transistor, the round solid core is not an optimized geometry for semiconductor materials due to its limited specific surface area. Thus, the thin-film configuration is also frequently used for improving device performance [59]. Figure 3(c) shows a photodetecting fiber integrating two layers of a thin-film semiconductor and eight electrodes for lensless imaging [60]. Moreover, by alternating the thickness and components of the outer semiconducting layer, wavelength discrimination could be achieved from the photocurrent ratios of the inner layer and outer layer (Figure 3(d)). Besides, the incident angle and color of the light could be figured out by adjusting the configuration of electrodes and semiconducting layers.

Since the polymers are easy to handle and process, multilayered structures could be conveniently realized in rectangular fibers by stacking different materials layer by layer for various applications, including energy storage [61, 62], acoustics [63], and actuator [64]. As shown in Figure 3(e), a multilayer structure of carbon-loaded polyethylene (CPE) and piezoelectric material poly(vinylidene fluoride trifluoroethylene) (P(VDF-TrFE)) is constructed in polycarbonate (PC) cladding [63]. This large active area multilayered structure allows the acoustic fiber to have an enhanced piezoelectric performance, indicating the opportunities in large-area conformal acoustic emission and sensing devices. Similarly, Figure 3(f) shows an energy storage fiber developed by folding multiple bilayers comprising PVDF as the dielectric layer and CPE as the electrode layer [61]. This capacitive response reached 20 kHz, and the capacitance increased to 47 nF/m

when six folds of the PVDF layer were integrated into a single fiber. The capacitance was further increased to 100 nF/m by a Swiss roll structure cylindrical fiber (Figure 3(g)).

Additionally, a number of thermally drawn polymer fibers with unique structures have been demonstrated for special applications [28, 65–67]. For example, a complex structure incorporating two photodetecting units and a hollow core is built inside a fiber for chemical sensing, as shown in the schematic in Figure 3(h) [28]. The inner surface of the hollow fiber is coated with a chemiluminescent material. Therefore, when the hazardous vapors enter the hollow core, light will be emitted from the chemiluminescent material and detected by the photodetecting units as sketched in Figure 3(i). This work achieved a high concentrate resolution of 10 ppb, paving the way for remote and large-area chemical sensing. Also, a microstructured fiber with a liquid metal electrode and four carbon-loaded polyethylene (CPE) domains encapsulated in a hollow-core SEBS matrix is demonstrated in Figure 3(j) [68]. CPE is a conductive polymer that served as electrodes. When a localized pressure is applied to the fiber, two CPE domains will get in contact. Hence, the resistance between the two electrodes at the fiber end can be measured. After the relationship between the distance and the resistance is calibrated, the location of the pressed point can be identified by the measured resistance. And the direction of the pressure can be determined from the three CPE domains at different positions (Figure 3(k)). Moreover, the amplitude of the pressure can be informed by the deformation of the liquid metal electrode. Thus, the direction, amplitude, and position of external pressure could be detected simultaneously through this microstructured fiber. A multimaterial fiber with irregular microfluidic channels for live and dead cell separation is displayed in Figures 3(l) and 3(m) [65]. Taking advantage of the ability to create arbitrary microchannel cross sections, this microfluidic fiber shows great potential in electrowetting, electro-taxis, and other microfluidic devices for blood capillaries and vascular transport tissues. Moreover, the control of the thermal drawing technique over fiber structure is not only limited to the geometry of each domain in the fiber. The microscopic structure of the domain is also adjustable. As shown in Figures 3(n) and 3(o), porous structure has been achieved via thermally induced phase separation during the thermal drawing process [69]. And freestanding porous fiber with different shapes can be obtained after removing the fiber cladding. All these functional structures for intriguing applications can be credited to the high flexibility in designing the inner structure of the thermally drawn fibers, revealing a future in multifunctional fibers and wearable electronics.

5. Breaking the Axial Symmetry of Thermally Drawn Fibers

During a typical thermal drawing process, all the structures and materials in the preform will be stretched to a fiber. Such an elongation process will lead to a continuous and uniform fiber with axial symmetry; i.e., the cross-sectional structure of the fiber will remain unchanged regardless of the cut-plane position. Although the high uniformity along the fiber axial

FIGURE 3: Various functional structures of thermally drawn multimaterial fibers. (a, b) An ovonic memory switching fiber with core/cladding configuration. Reproduced with permission. Copyright 2011, Wiley-VCH [55]. (c, d) A photodetecting fiber with thin-film functional material. Reproduced with permission. Copyright 2009, American Chemical Society [60]. (e) An acoustic fiber with a multilayered structure. Reproduced with permission. Copyright 2012, Wiley-VCH [63]. (f, g) An energy storage fiber with a multilayered structure (Scale bars, top: $300\ \mu\text{m}$, bottom: $20\ \mu\text{m}$). Reproduced with permission. Copyright 2013, AIP Publishing [61]. (h, i) A chemical sensing fiber with a complex inner structure. Reproduced with permission. Copyright 2012, Wiley-VCH [28]. (j, k) A pressure sensing fiber with a liquid metal electrode and four CPE domains encapsulated in a hollow-core SEBS matrix. Reproduced with permission. Copyright 2018, Wiley-VCH [68]. (l, m) A microfluidic fiber with irregular microchannels. Reproduced with permission. Copyright 2018, National Academy of Sciences [65]. (n, o) Porous fibers with different geometries. Reproduced under the terms of the Creative Commons Attribution license (CC BY 4.0). <https://creativecommons.org/licenses/by/4.0/> [69].

direction is a magnificent advantage of thermally drawn fibers to ensure reliable production and stable performance, it also brings some limitations in certain applications where

localized information along the fiber is needed, or multiple functional units are needed to be integrated along the fiber axial direction. Therefore, to make full use of the fiber length,

FIGURE 4: Approaches to fabricating axial asymmetric fibers. (a) Plateau-Rayleigh instability-induced breakup for sphere fabrication and device assembly. Reproduced under the terms of the Creative Commons Attribution license (CC BY 4.0). <https://creativecommons.org/licenses/by/4.0/> [70]. Reproduced with permission. Copyright 2016, Wiley-VCH [76]. (b) In-fiber particle manipulation based on the Marangoni convection. (c) Heterojunction formed in solid silica fiber via particle manipulation. Reproduced under the terms of the Creative Commons Attribution license (CC BY 4.0). <https://creativecommons.org/licenses/by/4.0/> [77]. (d) Laser recrystallization process for SnSe fiber. Reproduced with permission. Copyright 2020, Wiley-VCH [73]. (e) Cold drawing process for controlled fragmentation of multimaterial fibers. (f) Glass film from the fiber before cold drawing. (g) Glass film from the fiber after cold drawing. Reproduced with permission. Copyright 2016, published by Springer Nature [74].

create novel micro/nanostructures, and fabricate unique devices, numerous attempts have been made to break the axial symmetry of thermally drawn fibers, such as the introduction of Plateau-Rayleigh instability [70–72], laser recrystallization [73], cold drawing [74], and convergence thermal drawing [75].

Kaufman et al. reported a postprocessing approach to introduce Plateau-Rayleigh instability for breaking the axial symmetry of thermally drawn fibers [71]. This process starts with fabricating an axially uniform fiber with a core-cladding structure through the thermal drawing process. The fiber is then heated above the glass transition temperature of the cladding material by being fed into the furnace at a constant speed. During the heating process, the cladding material will become soft, and Plateau-Rayleigh instability-induced breakup will occur in the molten core material driven by the surface tension, forming a series of spheres in the fiber core. And spheres with different sizes and periods can be precisely controlled by adjusting the feeding speed and core diameter. This process can produce micro/nanospheres at high scalability by incorporating a high density of fiber cores in one preform. Thus, large numbers of spheres could be produced from the breakup simultaneously when heated in the furnace. Moreover, structured composite spheres such as core-shell spheres, “Janus” spheres, and multisectioned

spheres could be achieved by adjusting the core structure accordingly. However, the Plateau-Rayleigh instability-induced breakup from isothermal heating will result in a series of “satellite” spheres, which are much smaller than the designed sphere size, leading to limited sphere uniformity. Using localized heat sources such as flame and laser beam could address this issue [19, 76]. As shown in Figure 4(a), the localized flame could generate a gradient heating zone with a precisely controlled position instead of a large isothermal heating area. As a result, uniform spheres are fabricated in the fiber core without “satellite” spheres [70]. Furthermore, by constructing a multicore structure with different materials in the fiber, the selective breakup of the fiber cores could be achieved [76]. As displayed at the bottom of Figure 4(a), germanium (Ge) is sandwiched between two platinum (Pt) cores. As the melting temperature of Pt is much higher than that of Ge, only Ge core will break up and contact the two Pt cores after being heated, forming a series of metal-semiconductor-metal device architecture. These works exhibit numerous potential applications such as photodetection, drug delivery, and tunable optical scattering.

Besides the particle size, composite, and structure, the position of the in-fiber particles is also designable. Zhang et al. demonstrated an in-fiber particle manipulation based on the Marangoni convection in 2019 (Figure 4(b)) [77].

When a carbon dioxide (CO_2) laser beam is focused on the upper surface of the fiber, a temperature gradient, as well as surface tension gradient, will be generated. As the silica cladding is softened under the high temperature, the particles migrate along with the softened silica towards the heated point driven by the surface tension gradient. The moving direction and velocity can be precisely controlled by the laser direction and power. This in-fiber particle manipulation approach could be used for in-fiber device assembly. As shown in Figure 4(c), a heterojunction is formed by moving a silicon (Si) particle and a Ge particle into contact. A clear rectifying current-voltage (IV) curve is measured to reveal their stable contact, showing the perspective of the in-fiber assembly of 3D functional structures. Also, the crystal structure of the fiber core could be engineered by the laser beam [73]. As sketched in Figure 4(d), a thermoelectric material tin selenide (SnSe) core in a thermally drawn fiber is successfully recrystallized by CO_2 laser annealing from as-drawn polycrystalline to single crystalline. The recrystallized single-crystal SnSe fiber core shows superior thermoelectric properties. The ZT value is enhanced to 2 at 862 K. This approach enables more possibilities in fabricating high-performance single-crystal semiconductors in fiber-based devices.

The axial symmetry of the thermally drawn fiber can also be broken through cold drawing [74]. As shown in Figure 4(e), when a rectangular fiber with a brittle glass thin film and polymer cladding is gradually stretched, a necking appears and propagates along the fiber. The original thin film will be fragmented into well-ordered stripes progressively, as shown in the SEM (scanning electron microscope) images of the intact thin film and fragmented film after the cold drawing in Figures 4(f) and 4(g). This cold drawing process is reversible. And it is applicable to other fiber geometries, including rectangle, triangle, and cylinder, suggesting the potential applications in tuning optical properties of composite structure, large-area metasurface, and mass production of micro/nanoparticles.

Besides these postprocess approaches, a recently developed convergence thermal drawing technique has achieved drawing axial asymmetric fiber directly [75]. This technique includes rigid commercial semiconducting devices in the preform at the prescribed position. And tungsten wires are fed into the channels continuously during the thermal drawing process. As the lateral size reduced during the neckdown process, the wires and commercial devices will be squeezed together and achieve electrical contact. Therefore, a series of commercial devices can be incorporated into fibers at discrete positions and function well. This convergence thermal drawing process bridges the thermal drawing technique and the numerous planar semiconductor devices, providing a path to large-scale integration of functional devices in fibers.

6. Surface Structured Fibers Drawn from Patterned Preforms

So far, we have discussed various functional structures inside multimaterial fibers for numerous applications. Beyond the inner structure, creating surface structure could also endow thermally drawn fibers with many other unique functional-

ties, e.g., hydrophobic surface, antimicrobial effect, nerve guidance scaffolds, and coloration [78–80]. Therefore, several attempts have been reported to create surface patterns on thermally drawn fibers by far [81–86].

The fabrication processes of these fibers are quite similar. They usually start from etching grooves on a macroscopic preform through machining, laser etching, or soft lithography. Then, the patterned preform is applied to the thermal drawing process. During this process, the macroscopic preform will be elongated to a microscopic fiber, and the width of the grooves will be scaled down along with the preform, as sketched in Figure 5(a) [82]. As a result, the patterned cylindrical preform is drawn into a star-shaped fiber with a tunable diameter; i.e., one-directional microgrooves along fiber axial direction are achieved on the entire fiber surface (Figure 5(b)). And the pattern size can be controlled by alternating the preform pattern or adjusting the drawing parameters, including preform feeding speed and fiber drawing speed. Surface patterns on rectangular fibers are also reported. As shown in the SEM images in Figures 5(c)–5(e), by thermally drawing a patterned polymer bar, microstructures with the size down to several micrometers is created on a fiber surface [83]. Moreover, this process can create patterns in the inner surface of hollow fiber [84]. Two machined half-preforms are prepared followed by consolidating to form a hollow preform with inner surface patterns. And inner surface patterns with different sizes are achieved after the thermal drawing process.

Applications of the surface patterned fibers mentioned above are also demonstrated in previous works. The microgrooves could enhance the hydrophobicity of the polyethyleneimine (PEI) fiber surface [82]. As shown in Figure 5(f) (i) and (iii), the contact angle of water on the star-shaped PEI fiber is larger than that on the smooth fiber, indicating better hydrophobicity. Similarly, after a layer of PDA is coated on both smooth PEI fiber and star-shaped PEI fiber, the fibers become hydrophilic. Figure 5(f) (ii) and (iv) show that the contact angle of water on smooth PDA-coated fiber is 32° while it reaches 0° on star-shaped PDA-coated fiber. Moreover, the one-directional surface grating will lead to anisotropic wetting property; i.e., the measured contact angle is dependent on the observation direction. For the hydrophobic fibers, the contact angle measured perpendicular to the fiber axial direction is larger than that in the other direction. Such anisotropic wetting property and superhydrophilic surface enable the star-shaped PDA-coated fiber to have a promising application in microfluidics. As demonstrated in Figure 5(g), a fiber array is built, and several microfluidic channels filled with different colored water are formed. The water is transported along the channel very fast, and no intermixing is observed. Furthermore, several microfluidic networks have been constructed for connections, bridges, switches, and diagnostic devices. Additionally, similar demonstrations are also exhibited for surface patterned rectangular fibers. These demonstrations reveal the opportunities of surface patterned fibers in tuning the liquid behavior on large areas and flexible systems.

The periodic microgrooves on the fiber surface could also act as diffraction grating [83]. When the surface patterned

FIGURE 5: Surface patterned thermally drawn fibers and their applications. (a) Schematic of thermally drawn fibers with microgrooves. (b) SEM image of round fibers with microgrooves. (c–e) SEM images of microgrooves on rectangular fibers. (f) Wetting properties of smooth fibers and star-shaped fibers with and without PDA coating. (g) Microfluidic channels constructed from surface patterned fibers. (h–j) The structural coloration of surface patterned fibers. (k, l) Surface patterned fibers served as diffraction gratings. (a, b, f, g) Reproduced with permission. Copyright 2014, Wiley-VCH [82]. (c–e, h–l) Reproduced with permission. Copyright 2017, Wiley-VCH [83, 86].

fiber surface is illuminated by incandescent light, the diffraction grating will split the light with different wavelengths. Thus, the light with different wavelengths will be reflected in different directions. As shown in the photos in Figures 5(h) and 5(i), when observing from different directions, different colors will appear on the surface patterned fiber. And a colorful diffraction pattern will appear if the fiber is woven into a fabric, achieving structural coloration (Figure 5(j)). Likewise, when monochromatic light is incident on the grating, the transmitted light will be split and travel in different directions according to the following equation:

$$n\lambda = D \sin \alpha, \quad (2)$$

where n is the diffraction order, λ is the wavelength, D is the grating period, and α is the diffraction angle. Thus, fiber with a smaller groove period will lead to larger different angles, which is observed in the experimental results shown in Figures 5(k) and 5(l).

Also, the microgrooves can be fabricated on the inner surface of a hollow fiber. A previous study has shown that a series of inner surface patterned fibers are employed as nerve guidance scaffolds [84]. And the influence of scaffold geometry and sizes on neurite growth could be conveniently investigated owing to the advantage of the thermal drawing technique in fiber structure control. These diverse applications expose a broad perspective of surface patterned fibers.

7. Nanoscale and All-Directional Surface Patterned Fibers

Although different surface structured thermally drawn fibers have been fabricated for various applications as discussed above, these fabrication approaches are only compatible with creating surface grooves with a resolution of several micrometers.

To further improve the pattern resolution, an inherent limitation, polymer reflow, has to be addressed. Polymer reflow driven by surface tension occurs when a preform with an uneven surface is heated above its glass transition temperature. As the surface tension always tends to smoothen the

uneven surface, the resulting pattern on the fiber surface might be heavily distorted compared to its initial design, especially for a nanoscale pattern. To address this limitation, Nguyen-Dang et al. have studied this reflow process by modeling the underlying flowing mechanism [85, 86]. To simplify the model without losing the generality, they assume that the surface structure on the preform/fiber has the mathematical form of a sinusoidal function (one harmonic): $y^s(x) = d + h \sin((2\pi/\lambda)x)$, where d is the average thickness of the preform and h and λ are the amplitude and the period of the perturbation, respectively, both usually much smaller than the thickness of the preform: $h, \lambda \ll d$. Also, the deformation of the structure during the fiber drawing process is decoupled into two mechanisms: the scaling deformation due to the drawing process (scaling deformation) and the thermal deformation of the microstructure (reflow deformation). In this model, the differential dh representing the change in structure height of the surface pattern at a position z along the fiber axial direction is divided into two parts, i.e., the scaling deformation dh_{sc} caused by the thermal drawing process, which is the ideal case for the thermal drawing process, and the reflow deformation dh_{re} driven by surface tension.

$$dh = dh_{sc} + dh_{re}. \quad (3)$$

According to mass conservation and assuming that the polymer is incompressible, the volume flow through the cross section at position z and $z + dz$ should be the same. Thus, the scaling deformation dh_{sc} can be calculated.

$$dh_{sc} = -\frac{1}{2} \frac{h}{v} dv, \quad (4)$$

where v is the local drawing speed at position z . As the polymer is drawn at a high viscosity (usually 10^4 to 10^8 Pa*s), the Reynolds number of the polymer is estimated to be very small. Thus, the polymer could be considered as a Newtonian fluid. For ease of calculation, the surface pattern is assumed to be of sinusoidal shape with only one harmonic. And the reflow deformation dh_{re} could then be obtained by solving the Navier-Stokes equation.

$$dh_{re} = -\frac{\pi\gamma h}{\eta\lambda} dt = -\frac{\pi\gamma h}{\eta\lambda} \frac{dz}{v}, \quad (5)$$

where γ and η are the surface tension and viscosity of the polymer, respectively, and λ is the period of the sinusoidal surface pattern. Noticing that the deformation only occurs at the neckdown region in the furnace with a length of L , the final pattern height $h(L)$ could be obtained by combining equations (3)–(5) followed by integrating from $z = 0$ to $z = L$.

$$h(L) = h_0 \left(\frac{v_f}{V_0} \right)^{-(1/2)} \exp \left(\int_0^L -\pi \frac{\gamma}{\eta\lambda} \frac{1}{v} dz \right). \quad (6)$$

In this equation, the first part, $f_{sc} = (v_f/V_0)^{-(1/2)}$, is the scale-down ratio of the thermal drawing process. And the

second part, $\exp \left(\int_0^L -\pi(\gamma/\eta\lambda)(1/v)dz \right)$, represents the contribution of surface tension-induced polymer reflow, indicating that the polymer reflow will be enhanced exponentially with the increase in surface tension or decrease in pattern size. The reflow factor could be defined as $f_{re} = 1 - \exp \left(\int_0^L -\pi(\gamma/\eta\lambda)(1/v)dz \right)$. It varies from 0 to 1, where a value that tends to 0 means that the polymer reflow is negligible and the surface structure has no distortion, while a value that tends to 1 means that the polymer reflows heavily and the surface structure is totally collapsed during the thermal drawing process. Therefore, to achieve a smaller pattern size, lower surface tension is required to maintain a small value of the reflow factor.

The experimental verification is then performed. As shown in Figures 6(a) and 6(b), a patterned PC preform and a preform with patterned PC/CPE interface are prepared for the thermal drawing process. As the surface tension of PC is about one order higher than that of the PC/CPE interface [87], the reflow factor value of PC is much larger than that of PC/CPE under the same drawing condition, as plotted in Figure 6(c). For fibers drawing from the PC preform, both surface patterns with the periods of $2\mu\text{m}$ and $10\mu\text{m}$ are heavily distorted (top of Figure 6(c)). For fibers drawing from the PC/CPE preform, the PC layers are peeled off from the CPE layer after the thermal drawing process. Thus, PC fibers with exposed surface patterns are achieved, which show much smaller distortion with similar pattern periods (bottom of Figure 6(c)). Through the same process, a more complex hierarchical surface pattern on PC fiber is successfully fabricated, reaching a pattern resolution in the sub-micrometer level, as shown in Figure 6(d) (i). Similarly, high-resolution surface structure can also be achieved on cylindrical fibers (Figure 6(d) (ii) and (iii)). The smallest feature size of around 100 nm is demonstrated by constructing a poly(methyl methacrylate)/polycarbonate (PMMA/PC) interface, which has a very low interfacial tension of 0.39 mN/m [85].

However, constructing low interfacial tension in preform sacrifices the flexibility in designing the fiber's inner structure. Furthermore, because of the elongation during the thermal drawing process, all the exhibited surface patterns on fibers are limited in one-directional structure along the fiber axial direction, which essentially hinders the development of patterned fibers.

To create high-resolution surface patterns in arbitrary directions, the direct imprinting in thermal drawing (DITD) technique is proposed to combine the thermal drawing technique and nanoimprinting [81]. As shown in the schematic in Figure 6(e), a pair of rollers with surface patterns is placed right below the furnace. Once the fiber is drawn out of the furnace from the neckingdown area, it is directly pressed by the patterned rollers. Thus, reverse patterns will be created on both fiber surfaces as the temperature of the thermoplastic fiber is still above its glass transition temperature. Also, during the imprinting process, the temperature of the fiber will drop significantly as the roller is at a low temperature. Such a temperature drop can greatly reduce the reflow, leading to a high-fidelity pattern on the fiber surface. The SEM image in Figure 6(f) confirms that a regular 2D dot array is formed

FIGURE 6: Thermally drawn fibers with nanoscale and all-directional surface patterns. Thermal drawing process of (a) a PC preform with a patterned surface and (b) a preform with patterned PC/CPE interface. (c) Reflow factor of the patterned surface PC and the patterned PC/CPE interface. The two SEM images on top show the distorted surface pattern on the fiber drawn from the PC perform, while the two SEM images at the bottom exhibit a much smaller pattern distortion on the fiber surface drawn from the PC/CPE preform. Scale bars in the top left and bottom left: $2\ \mu\text{m}$. Scale bars in the top right and bottom right: $20\ \mu\text{m}$. (d) SEM images of the hierarchical patterns on the fiber surface. Reproduced with permission. Copyright 2017, Wiley-VCH [86]. Reproduced with permission. Copyright 2019, AIP Publishing [85]. (e) Schematic of the DITD technique. (f) 2D dot array on the fiber surface. (g) Interference pattern when the fiber is illuminated by a white supercontinuum laser. (h) 300-meter long fully patterned fiber collected on a cylindrical bobbin. (i) SEM images and the corresponding local electric field spatial distributions of the round nanopatterns with different spacings on fiber surfaces. Scale bars for pattern 1: $300\ \text{nm}$. Scale bars for pattern 2: $150\ \text{nm}$. (j) Dark-field scattering spectral measurement and simulated scattering cross section of the fibers with two patterns in (i). Reproduced under the terms of the Creative Commons Attribution license (CC BY 4.0). <https://creativecommons.org/licenses/by/4.0/> [81].

on the fiber surface after being pressed by rollers patterned with a 2D hole array. When white light laser illuminates this fiber, a clear interference pattern appears (Figure 6(g)), revealing the high quality of the pattern on the fiber surface. Through this DITD technique, a 300-meter-long continuous fiber is obtained with a surface pattern covered on the entire surface, as shown in the photos in Figure 6(h). By changing the templates on the rollers, a wide range of regular patterns

in different directions and irregular patterns and customized letters can be created on the surface of fibers with various materials. As the feature size of the surface pattern reaches as small as tens of nanometers, several surface patterned fibers with different nanostructures are fabricated, as demonstrated in Figure 6(i). The plasmonic behaviors of the fiber with round nanopatterns are studied. And the experimental results in Figure 6(j) agree well with the simulated results.

Moreover, a multimaterial fiber with surface microstructure is fabricated for energy harvesting. The performance of the surface patterned fiber is much higher than that of the flat fiber. And a multipoint touch sensing fabric is successfully constructed. This DITD technique avoids the elongation of surface patterns and greatly reduces the reflow, representing the bright future in functional fibers and wearable electronics.

8. Conclusion and Outlook

The high scalability, uniformity, and material and structure compatibility of the thermal drawing technique enable a wide range of intriguing applications based on multimaterial fibers. In this review article, we have discussed various functional structures constructed in multimaterial fibers for various applications, including optoelectronics, electronics, micro/nanofabrication, and neural interfaces. Specifically, we firstly introduced some commonly used structures for optical fibers. Then, we presented some typical structures and more complex and special structures achieved in multimaterial fibers. Next, we discussed the efforts towards breaking the axial symmetry of thermally drawn fibers. At last, we summarized previous works on creating structures on fiber surfaces. These functional structures could serve as strong supports to the functional materials for realizing fiber functionalities.

Although countless thermally drawn multimaterial fibers with various functional structures have been demonstrated, the development of multimaterial fibers is still in its early stage, and more studies are needed to achieve deeper understandings of the underlying science, including rheology, thermodynamics, fluid mechanics, and material processing. These fundamental studies could greatly help researchers to revisit and improve the current progress, including developing thermoplastic materials with ideal rheological properties to promote structural accuracy and finding novel materials to expand the functionalities of multimaterial fibers. Also, semiconductors, the key materials of modern industry, should be further explored for incorporated into functional fibers. Previous works have shown various semiconductor fibers and exhibited many fascinating applications based on the core-cladding structure [88–95]. Further developments could be made in employing new semiconductors (such as organic semiconductors) and combining them with well-designed fiber structures and electrode configurations to achieve better performance and more functionalities. Moreover, integrating disparate functions in a single fiber by combining surface patterns, functional materials, and fiber structures is highly demanded. Noticing that different surface patterns could realize different functions and the created surface pattern only alters the surface of the fibers without affecting inner material and architecture, various functionalities can be brought to current functional fibers as additional values. Therefore, the tremendous combinations of surface patterns, functional materials, and fiber architectures represent the countless possibilities of multifunctional fibers. Furthermore, modern textile technology can be applied to thermally drawn fibers for producing highly integrated func-

tional fabrics at industrial scales. And the ability to incorporate different functional fibers will lead to multifunctional fabrics. Therefore, we would like to invite industrial and academic researchers in related fields to join and collaborate on this promising topic. We can envision that the thermally drawn multimaterial fibers will open a new era of wearable devices and smart textiles.

Conflicts of Interest

The authors declare no competing interests.

Authors' Contributions

Zhe Wang and Mengxiao Chen contributed equally to this work.

Acknowledgments

This work was supported by the Singapore Ministry of Education Academic Research Fund Tier 2 (MOE2019-T2-2-127 and T2EP50120-0005), A*STAR under AME IRG (A2083c0062), the Singapore Ministry of Education Academic Research Fund Tier 1 (RG90/19 and RG73/19), and the Singapore's National Research Foundation Competitive Research Program (NRF-CRP18-2017-02). This work was also supported by Nanyang Technological University.

References

- [1] J. C. Splitstoser, T. D. Dillehay, J. Wouters, and A. Claro, "Early pre-hispanic use of indigo blue in Peru," *Science Advances*, vol. 2, no. 9, article e1501623, 2016.
- [2] N. Cui, J. Liu, L. Gu, S. Bai, X. Chen, and Y. Qin, "Wearable triboelectric generator for powering the portable electronic devices," *ACS Applied Materials & Interfaces*, vol. 7, no. 33, pp. 18225–18230, 2015.
- [3] L. Gu, J. Liu, N. Cui et al., "Enhancing the current density of a piezoelectric nanogenerator using a three-dimensional intercalation electrode," *Nature Communications*, vol. 11, no. 1, p. 1030, 2020.
- [4] L. Lao, L. Fu, G. Qi, E. P. Giannelis, and J. Fan, "Superhydrophilic wrinkle-free cotton fabrics via plasma and nanofluid treatment," *ACS Applied Materials & Interfaces*, vol. 9, no. 43, pp. 38109–38116, 2017.
- [5] T. L. Andrew, L. Zhang, N. Cheng et al., "Melding vapor-phase organic chemistry and textile manufacturing to produce wearable electronics," *Accounts of Chemical Research*, vol. 51, no. 4, pp. 850–859, 2018.
- [6] Z. Wen, M.-H. Yeh, H. Guo et al., "Self-powered textile for wearable electronics by hybridizing fiber-shaped nanogenerators, solar cells, and supercapacitors," *Science Advances*, vol. 2, no. 10, article e1600097, 2016.
- [7] Y. Qin, X. Wang, and Z. L. Wang, "Microfibre–nanowire hybrid structure for energy scavenging," *Nature*, vol. 451, no. 7180, pp. 809–813, 2008.
- [8] J. Liu, L. Gu, N. Cui et al., "Core-shell fiber-based 2d woven triboelectric nanogenerator for effective motion energy harvesting," *Nanoscale Research Letters*, vol. 14, no. 1, p. 311, 2019.
- [9] Y. P. Wang, L. Xiao, D. N. Wang, and W. Jin, "Highly sensitive long-period fiber-grating strain sensor with low

- temperature sensitivity," *Optics Letters*, vol. 31, no. 23, pp. 3414–3416, 2006.
- [10] G. Loke, W. Yan, T. Khudiyev, G. Noel, and Y. Fink, "Recent progress and perspectives of thermally drawn multimaterial fiber electronics," *Advanced Materials*, vol. 32, no. 1, p. 1904911, 2019.
 - [11] O. Shapira, K. Kuriki, N. D. Orf et al., "Surface-emitting fiber lasers," *Optics Express*, vol. 14, no. 9, pp. 3929–3935, 2006.
 - [12] B. A. Flusberg, E. D. Cocker, W. Piyawattanametha, J. C. Jung, E. L. M. Cheung, and M. J. Schnitzer, "Fiber-optic fluorescence imaging," *Nature Methods*, vol. 2, no. 12, pp. 941–950, 2005.
 - [13] N. M. Y. Zhang, M. Qi, Z. Wang et al., "One-step synthesis of cyclodextrin-capped gold nanoparticles for ultra-sensitive and highly-integrated plasmonic biosensors," *Sensors and Actuators B: Chemical*, vol. 286, pp. 429–436, 2019.
 - [14] Z. Chun-Liu, Y. Xiufeng, M. S. Demokan, and W. Jin, "Simultaneous temperature and refractive index measurements using a 3/spl deg/ slanted multimode fiber Bragg grating," *Journal of Lightwave Technology*, vol. 24, no. 2, pp. 879–883, 2006.
 - [15] W. Yan, A. Page, T. Nguyen-Dang et al., "Advanced multimaterial electronic and optoelectronic fibers and textiles," *Advanced Materials*, vol. 31, no. 1, article e1802348, 2019.
 - [16] W. Yan, Y. Qu, T. D. Gupta et al., "Semiconducting nanowire-based optoelectronic fibers," *Advanced Materials*, vol. 29, no. 27, p. 1700681, 2017.
 - [17] W. Yan, C. Dong, Y. Xiang et al., "Thermally drawn advanced functional fibers: new frontier of flexible electronics," *Materials Today*, vol. 35, pp. 168–194, 2020.
 - [18] A. C. Peacock and N. Healy, "Semiconductor optical fibres for infrared applications: a review," *Semiconductor Science and Technology*, vol. 31, no. 10, p. 103004, 2016.
 - [19] J. Zhang, K. Li, T. Zhang et al., "Laser-induced in-fiber fluid dynamical instabilities for precise and scalable fabrication of spherical particles," *Advanced Functional Materials*, vol. 27, no. 43, p. 1703245, 2017.
 - [20] M. Du, L. Huang, J. Zheng et al., "Flexible fiber probe for efficient neural stimulation and detection," *Advanced Science*, vol. 7, no. 15, p. 2001410, 2020.
 - [21] W. Yan, I. Richard, G. Kurtuldu et al., "Structured nanoscale metallic glass fibres with extreme aspect ratios," *Nature Nanotechnology*, vol. 15, no. 10, pp. 875–882, 2020.
 - [22] M. Zhu, X. Wang, Z. Pan et al., "Fabrication of an IR hollow-core Bragg fiber based on chalcogenide glass extrusion," *Applied Physics A*, vol. 119, no. 2, pp. 455–460, 2015.
 - [23] D. Shahriari, G. Loke, I. Tafel et al., "Scalable fabrication of porous microchannel nerve guidance scaffolds with complex geometries," *Advanced Materials*, vol. 31, no. 30, p. 1902021, 2019.
 - [24] L. Xavier and D. Elangovan, "Effective parameters for improving deep hole drilling process by conventional method - a review," *International journal of engineering research and technology*, vol. 2, 2013.
 - [25] Y. N. Zhang, K. Li, L. L. Wang et al., "Casting preforms for microstructured polymer optical fibre fabrication," *Optics Express*, vol. 14, no. 12, pp. 5541–5547, 2006.
 - [26] W. Talataisong, R. Ismael, T. H. R. Marques et al., "Mid-IR hollow-core microstructured fiber drawn from a 3d printed PETG preform," *Scientific Reports*, vol. 8, no. 1, p. 8113, 2018.
 - [27] R. Mossadegh, J. S. Sanghera, D. Schaafsma et al., "Fabrication of single-mode chalcogenide optical fiber," *Journal of Lightwave Technology*, vol. 16, no. 2, pp. 214–217, 1998.
 - [28] A. Gumennik, A. M. Stolyarov, B. R. Schell et al., "All-in-fiber chemical sensing," *Advanced Materials*, vol. 24, no. 45, pp. 6005–6009, 2012.
 - [29] K. Cook, G. Balle, J. Canning et al., "Step-index optical fiber drawn from 3d printed preforms," *Optics Letters*, vol. 41, no. 19, pp. 4554–4557, 2016.
 - [30] C. Hou, X. Jia, L. Wei et al., "Crystalline silicon core fibres from aluminium core preforms," *Nature Communications*, vol. 6, no. 1, p. 6248, 2015.
 - [31] N. D. Orf, O. Shapira, F. Sorin et al., "Fiber draw synthesis," *Proceedings of the National Academy of Sciences*, vol. 108, no. 12, pp. 4743–4747, 2011.
 - [32] W. A. Gambling, "The rise and rise of optical fibers," *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 6, no. 6, pp. 1084–1093, 2000.
 - [33] J. Mateo, M. A. Losada, and I. Garcés, "Global characterization of optical power propagation in step-index plastic optical fibers," *Optics Express*, vol. 14, no. 20, pp. 9028–9035, 2006.
 - [34] W. Jin, Y. Cao, F. Yang, and H. L. Ho, "Ultra-sensitive all-fibre photothermal spectroscopy with large dynamic range," *Nature Communications*, vol. 6, no. 1, p. 6767, 2015.
 - [35] J. M. Dudley and J. R. Taylor, "Ten years of nonlinear optics in photonic crystal fibre," *Nature Photonics*, vol. 3, no. 2, pp. 85–90, 2009.
 - [36] J. C. Knight, J. Arriaga, T. A. Birks, A. Ortigosa-Blanch, W. J. Wadsworth, and P. S. J. Russell, "Anomalous dispersion in photonic crystal fiber," *IEEE Photonics Technology Letters*, vol. 12, no. 7, pp. 807–809, 2000.
 - [37] X. L. Tan, Y. F. Geng, E. B. Li, W. N. Wang, P. Wang, and J. Q. Yao, "Characterization of bent large-mode-area photonic crystal fiber," *Journal of Optics a-Pure and Applied Optics*, vol. 10, no. 8, p. 085303, 2008.
 - [38] J. C. Knight, J. Broeng, T. A. Birks, and P. S. J. Russell, "Photonic band gap guidance in optical fibers," *Science*, vol. 282, no. 5393, pp. 1476–1478, 1998.
 - [39] P. Yeh, A. Yariv, and E. Marom, "Theory of Bragg fiber," *Journal of the Optical Society of America*, vol. 68, no. 9, pp. 1196–1201, 1978.
 - [40] B. Temelkuran, S. D. Hart, G. Benoit, J. D. Joannopoulos, and Y. Fink, "Wavelength-scalable hollow optical fibres with large photonic bandgaps for CO₂ laser transmission," *Nature*, vol. 420, no. 6916, pp. 650–653, 2002.
 - [41] K. Kuriki, O. Shapira, S. D. Hart et al., "Hollow multilayer photonic bandgap fibers for NIR applications," *Optics Express*, vol. 12, no. 8, pp. 1510–1517, 2004.
 - [42] R. R. Gattass, D. Rhonehouse, D. Gibson et al., "Infrared glass-based negative-curvature anti-resonant fibers fabricated through extrusion," *Optics Express*, vol. 24, no. 22, pp. 25697–25703, 2016.
 - [43] G. Vienne, Y. Xu, C. Jakobsen et al., "Ultra-large bandwidth hollow-core guiding in all-silica Bragg fibers with nano-supports," *Optics Express*, vol. 12, no. 15, pp. 3500–3508, 2004.
 - [44] G. B. Ren, P. Shum, L. R. Zhang, X. Yu, W. J. Tong, and J. Luo, "Low-loss all-solid photonic bandgap fiber," *Optics Letters*, vol. 32, no. 9, pp. 1023–1025, 2007.
 - [45] F. Poletti, M. N. Petrovich, and D. J. Richardson, "Hollow-core photonic bandgap fibers: technology and applications," *Nano*, vol. 2, no. 5–6, pp. 315–340, 2013.
 - [46] G. Benoit, S. D. Hart, B. Temelkuran, J. D. Joannopoulos, and Y. Fink, "Static and dynamic properties of optical

- microcavities in photonic bandgap yarns," *Advanced Materials*, vol. 15, no. 24, pp. 2053–2056, 2003.
- [47] A. M. Cubillas, M. Silva-Lopez, J. M. Lazaro, O. M. Conde, M. N. Petrovich, and J. M. Lopez-Higuera, "Methane detection at 1670-nm band using a hollow-core photonic bandgap fiber and a multiline algorithm," *Optics Express*, vol. 15, no. 26, pp. 17570–17576, 2007.
 - [48] F. Benabid, "Hollow-core photonic bandgap fibre: new light guidance for new science and technology," *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences*, vol. 364, no. 1849, pp. 3439–3462, 2006.
 - [49] G. T. Jasion, T. D. Bradley, K. Harrington et al., "Hollow core NANF with 0.28 dB/km attenuation in the C and L bands," in *Optical Fiber Communication Conference Postdeadline Papers 2020*, San Diego, California, 2020.
 - [50] M. Xu, F. Yu, and J. Knight, "Mid-infrared 1 W hollow-core fiber gas laser source," *Optics Letters*, vol. 42, no. 20, pp. 4055–4058, 2017.
 - [51] E. Lee, J. Luo, B. Sun et al., "45w 2 μ m nanosecond pulse delivery using antiresonant hollow-core fiber," in *2018 Conference on Lasers and Electro-Optics (CLEO)*, pp. 1-2, San Jose, CA, USA, 2018.
 - [52] X. L. Liu, W. Ding, Y. Y. Wang et al., "Characterization of a liquid-filled nodeless anti-resonant fiber for biochemical sensing," *Optics Letters*, vol. 42, no. 4, pp. 863–866, 2017.
 - [53] P. J. Roberts, F. Couny, H. Sabert et al., "Ultimate low loss of hollow-core photonic crystal fibres," *Optics Express*, vol. 13, no. 1, pp. 236–244, 2005.
 - [54] G. Tao, A. M. Stolyarov, and A. F. Abouraddy, "Multimaterial fibers," *International Journal of Applied Glass Science*, vol. 3, no. 4, pp. 349–368, 2012.
 - [55] S. Danto, Z. Ruff, Z. Wang, J. D. Joannopoulos, and Y. Fink, "Ovonic memory switching in multimaterial fibers," *Advanced Functional Materials*, vol. 21, no. 6, pp. 1095–1101, 2011.
 - [56] A. F. Abouraddy, O. Shapira, M. Bayindir et al., "Large-scale optical-field measurements with geometric fibre constructs," *Nature Materials*, vol. 5, no. 7, pp. 532–536, 2006.
 - [57] M. Bayindir, F. Sorin, A. F. Abouraddy et al., "Metal-insulator-semiconductor optoelectronic fibres," *Nature*, vol. 431, no. 7010, pp. 826–829, 2004.
 - [58] M. Bayindir, A. F. Abouraddy, J. Arnold, J. D. Joannopoulos, and Y. Fink, "Thermal-sensing fiber devices by multimaterial codrawing," *Advanced Materials*, vol. 18, no. 7, pp. 845–849, 2006.
 - [59] M. Bayindir, O. Shapira, D. Saygin-Hinczewski et al., "Integrated fibres for self-monitored optical transport," *Nature Materials*, vol. 4, no. 11, pp. 820–825, 2005.
 - [60] F. Sorin, O. Shapira, A. F. Abouraddy et al., "Exploiting collective effects of multiple optoelectronic devices integrated in a single fiber," *Nano Letters*, vol. 9, no. 7, pp. 2630–2635, 2009.
 - [61] G. Lestoquoy, N. Chocat, Z. Wang, J. D. Joannopoulos, and Y. Fink, "Fabrication and characterization of thermally drawn fiber capacitors," *Applied Physics Letters*, vol. 102, no. 15, p. 152908, 2013.
 - [62] T. Khudiyev, J. T. Lee, J. R. Cox et al., "100 m long thermally drawn supercapacitor fibers with applications to 3d printing and textiles," *Advanced Materials*, vol. 32, no. 49, p. 2004971, 2020.
 - [63] N. Chocat, G. Lestoquoy, Z. Wang, D. M. Rodgers, J. D. Joannopoulos, and Y. Fink, "Piezoelectric fibers for conformal acoustics," *Advanced Materials*, vol. 24, no. 39, pp. 5327–5332, 2012.
 - [64] T. Khudiyev, J. Clayton, E. Levy et al., "Electrostrictive micro-electromechanical fibres and textiles," *Nature Communications*, vol. 8, no. 1, p. 1435, 2017.
 - [65] R. Yuan, J. Lee, H.-W. Su et al., "Microfluidics in structured multimaterial fibers," *Proceedings of the National Academy of Sciences*, vol. 115, no. 46, pp. E10830–E10838, 2018.
 - [66] C. Dong, A. G. Page, W. Yan, T. Nguyen-Dang, and F. Sorin, "Microstructured multimaterial fibers for microfluidic sensing," *Advanced Materials Technologies*, vol. 4, no. 10, p. 1900417, 2019.
 - [67] G. Loke, R. Yuan, M. Rein et al., "Structured multimaterial filaments for 3d printing of optoelectronics," *Nature Communications*, vol. 10, no. 1, p. 4010, 2019.
 - [68] Y. Qu, T. Nguyen-Dang, A. G. Page et al., "Superelastic multimaterial electronic and photonic fibers and devices via thermal drawing," *Advanced Materials*, vol. 30, no. 27, p. 1707251, 2018.
 - [69] B. Grena, J.-B. Alayrac, E. Levy, A. M. Stolyarov, J. D. Joannopoulos, and Y. Fink, "Thermally-drawn fibers with spatially-selective porous domains," *Nature Communications*, vol. 8, no. 1, p. 364, 2017.
 - [70] A. Gumennik, L. Wei, G. Lestoquoy et al., "Silicon-in-silica spheres via axial thermal gradient in-fibre capillary instabilities," *Nature Communications*, vol. 4, no. 1, p. 2216, 2013.
 - [71] J. J. Kaufman, G. Tao, S. Shabahang et al., "Structured spheres generated by an in-fibre fluid instability," *Nature*, vol. 487, no. 7408, pp. 463–467, 2012.
 - [72] A. Gumennik, E. C. Levy, B. Grena et al., "Confined in-fiber solidification and structural control of silicon and silicon-germanium microparticles," *Proceedings of the National Academy of Sciences*, vol. 114, no. 28, pp. 7240–7245, 2017.
 - [73] J. Zhang, T. Zhang, H. Zhang et al., "Single-crystal SnSe thermoelectric fibers via laser-induced directional crystallization: from 1D fibers to multidimensional fabrics," *Advanced Materials*, vol. 32, article 2002702, 2020.
 - [74] S. Shabahang, G. Tao, J. J. Kaufman et al., "Controlled fragmentation of multimaterial fibres and films via polymer cold-drawing," *Nature*, vol. 534, no. 7608, pp. 529–533, 2016.
 - [75] M. Rein, V. D. Favrod, C. Hou et al., "Diode fibres for fabric-based optical communications," *Nature*, vol. 560, no. 7717, pp. 214–218, 2018.
 - [76] L. Wei, C. Hou, E. Levy et al., "Optoelectronic fibers via selective amplification of in-fiber capillary instabilities," *Advanced Materials*, vol. 29, no. 1, p. 1603033, 2017.
 - [77] J. Zhang, Z. Wang, Z. Wang, T. Zhang, and L. Wei, "In-fibre particle manipulation and device assembly via laser induced thermocapillary convection," *Nature Communications*, vol. 10, no. 1, p. 5206, 2019.
 - [78] D. Roe, B. Karandikar, N. Bonn-Savage, B. Gibbins, and J.-B. Roullet, "Antimicrobial surface functionalization of plastic catheters by silver nanoparticles," *Journal of Antimicrobial Chemotherapy*, vol. 61, no. 4, pp. 869–876, 2008.
 - [79] J. Sun, B. Bhushan, and J. Tong, "Structural coloration in nature," *RSC Advances*, vol. 3, no. 35, pp. 14862–14889, 2013.
 - [80] L. Feng, S. Li, H. Li et al., "Super-hydrophobic surface of aligned polyacrylonitrile nanofibers," *Angewandte Chemie International Edition*, vol. 41, no. 7, pp. 1221–1223, 2002.

- [81] Z. Wang, T. Wu, Z. Wang et al., "Designer patterned functional fibers via direct imprinting in thermal drawing," *Nature Communications*, vol. 11, no. 1, p. 3842, 2020.
- [82] A. Yildirim, M. Yunusa, F. E. Ozturk, M. Kanik, and M. Bayindir, "Surface textured polymer fibers for microfluidics," *Advanced Functional Materials*, vol. 24, no. 29, pp. 4569–4576, 2014.
- [83] T. Khudiyev, C. Hou, A. M. Stolyarov, and Y. Fink, "Sub-micrometer surface-patterned ribbon fibers and textiles," *Advanced Materials*, vol. 29, no. 22, p. 1605868, 2017.
- [84] R. A. Koppes, S. Park, T. Hood et al., "Thermally drawn fibers as nerve guidance scaffolds," *Biomaterials*, vol. 81, pp. 27–35, 2016.
- [85] T. Nguyen Dang, I. Richard, E. Goy, F. Sordo, and F. Sorin, "Insights into the fabrication of sub-100 nm textured thermally drawn fibers," *Journal of Applied Physics*, vol. 125, no. 17, p. 175301, 2019.
- [86] T. Nguyen-Dang, A. C. de Luca, W. Yan et al., "Controlled sub-micrometer hierarchical textures engineered in polymeric fibers and microchannels via thermal drawing," *Advanced Functional Materials*, vol. 27, no. 10, p. 1605935, 2017.
- [87] H. T. Pham and C. J. Carriere, "The effect of temperature on the interfacial tension of polycarbonate/polyethylene blends," *Polymer Engineering & Science*, vol. 37, no. 3, pp. 636–639, 1997.
- [88] T. Zhang, K. Li, J. Zhang et al., "High-performance, flexible, and ultralong crystalline thermoelectric fibers," *Nano Energy*, vol. 41, pp. 35–42, 2017.
- [89] T. Zhang, Z. Wang, B. Srinivasan et al., "Ultraflexible glassy semiconductor fibers for thermal sensing and positioning," *ACS Applied Materials & Interfaces*, vol. 11, pp. 2441–2447, 2018.
- [90] J. Ballato, T. Hawkins, P. Foy et al., "Silicon optical fiber," *Optics Express*, vol. 16, no. 23, pp. 18675–18683, 2008.
- [91] J. Ballato, T. Hawkins, P. Foy et al., "Glass-clad single-crystal germanium optical fiber," *Optics Express*, vol. 17, no. 10, pp. 8029–8035, 2009.
- [92] D. A. Coucheron, M. Fokine, N. Patil et al., "Laser recrystallization and inscription of compositional microstructures in crystalline SiGe-core fibres," *Nature Communications*, vol. 7, no. 1, p. 13265, 2016.
- [93] N. Healy, U. Gibson, and A. C. Peacock, "A review of materials engineering in silicon-based optical fibres," *Semiconductor Science and Technology*, vol. 33, no. 2, article 023001, 2018.
- [94] A. C. Peacock, J. Campling, A. F. J. Runge et al., "Wavelength conversion and supercontinuum generation in silicon optical fibers," *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 24, no. 3, pp. 1–9, 2018.
- [95] A. C. Peacock, U. J. Gibson, and J. Ballato, "Silicon optical fibres – past, present, and future," *Advances in Physics: X*, vol. 1, no. 1, pp. 114–127, 2016.
- [96] G. K. L. Wong, M. S. Kang, H. W. Lee et al., "Excitation of orbital angular momentum resonances in helically twisted photonic crystal fiber," *Science*, vol. 337, no. 6093, pp. 446–449, 2012.
- [97] R. Beravat, G. K. L. Wong, M. H. Frosz, X. M. Xi, and P. S. J. Russell, "Twist-induced guidance in coreless photonic crystal fiber: a helical channel for light," *Science Advances*, vol. 2, no. 11, article e1601421, 2016.
- [98] P. Zhao, Y. Zhao, H. Bao et al., "Mode-phase-difference photo-thermal spectroscopy for gas detection with an anti-resonant hollow-core optical fiber," *Nature Communications*, vol. 11, no. 1, p. 847, 2020.
- [99] J. R. Sparks, R. He, N. Healy et al., "Zinc selenide optical fibers," *Advanced Materials*, vol. 23, no. 14, pp. 1647–1651, 2011.