Review

Sol–Gel Routes toward Ceramic Nanofibers for High-Performance Thermal Management

Jing Zhang 1,2, Junxiong Zhang 1,* Qilong Sun 3, Xinli Ye 3, Xiaomin Ma 4 and Jin Wang 2,*

1 School of Textile and Clothing, Nantong University, Nantong 226019, China
2 Key Laboratory of Multifunctional Nanomaterials and Smart Systems, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China
3 School of Civil Aviation, Northwestern Polytechnical University, Xi’an 710072, China
4 National Equipment New Materials & Technology (Jiangsu) Co., Ltd., Suzhou 215101, China
* Correspondence: zhangjunxiong@ntu.edu.cn (J.Z.); jwang2014@sinano.ac.cn (J.W.)

Abstract: Ceramic-based nanofiber materials for high-performance thermal management have drawn increasing attention owing to their high-temperature resistance, efficient thermal insulation, superior mechanical flexibility, as well as excellent physical–chemical stability. We present an overview of the ceramic-based nanofiber obtained by sol–gel routes for high-performance thermal management, including the materials, the fabrication methods of the sol–gel route, and their application for thermal management. We first provide a brief introduction to the ceramic-based nanofibers. The materials and fabrication methods of the sol–gel route are further discussed in the second part, including the kinds of nanofibers such as oxide, carbide, and nitride, and the methods such as centrifugal spinning, electrospinning, solution blow spinning, and self-assembly. Finally, their application for thermal management is further illustrated. This review will provide some necessary suggestions to researchers for the investigation of ceramic-based nanofibers produced with the sol–gel route for thermal management.

Keywords: nanofiber; sol–gel route; thermal management; high-temperature resistance

1. Introduction

Ceramic-based fiber materials, especially the micron–nano-level ceramic fibers, have drawn increasing attention in recent years. Efforts toward developing ceramic-based fibers have been increasing for nearly a decade, dominated by research and application reports from China, accounting for 40% of the total publications among all countries [1].

The most common ceramic fibers are usually fabricated by the slurry method or molten liquid spinning, both methods utilizing a ceramic slurry made of a micron–nano-level ceramic particle as the precursor, the inherent properties of which, such as great hardness and brittleness of ceramic materials, lead to an insufficient toughness of the ceramic-based fiber materials, and seriously limit their applications. On the other hand, flexible ceramic fiber products have been in huge demand for high-performance thermal management in high temperatures, owing to their superior high-temperature resistance, great mechanical flexibility, and excellent chemical stability.

Researchers, therefore, have applied significant effort towards the preparation of flexible ceramic-based nanofibers, especially for two- or three-dimensional products, such as ceramic-based nanofiber films or aerogels, because they usually possess ultra-low density, high porosity, large specific surface area, high-temperature resistance, oxide resistance, and low thermal conductivity in wide temperature ranges. For the preparation of ceramic-based nanofibers, there are several methods: the slurry method, the chemical vapor deposition method, the polymer precursor conversion, the molten liquid spinning, and the sol–gel method, among which the sol–gel route method dominates due to its low
cost, low operating temperature, and excellent production efficiency. In addition, ceramic-based nanofibers have been widely applied due to their superior properties in the industries of gas filtration [2], sound absorption [3,4], thermal insulation [5–7], luminescence [8], microwave absorption [9], electromagnetic shielding [10], and others.

In this review, we summarized flexible ceramic-based nanofibers for the purpose of thermal management, including the preparation method, the materials, the thermal insulation mechanisms, and their applications. We first introduce the sol–gel routes of the ceramic-based nanofibers. Next, we briefly introduce the materials utilized in the fabrication of the ceramic-based nanofibers, including the oxides, carbides, and nitrides. Finally, applications of ceramic-based nanofibers in thermal management are discussed.

2. Nanofibers Prepared by Sol–Gel Routes

Nanofibers can be divided into two types: organic and inorganic, according to their chemical components. The organic nanofibers include biofibers such as cellulose-based fibers and protein fibers, and chemical fibers such as polyethylene (PE), polypropylene (PP), polyvinyl acetate (PVA), and polyvinyl chloride (PVC). Inorganic nanofibers include oxide fiber, carbide fibers, nitride fibers, and others. Owing to organic fibers’ inherent lack of high-temperature resistance, researchers aiming at developing nanofibers for high-temperature applications mainly focus on low-cost fabrication of the inorganic fibers, especially those which could be used in high-temperature conditions, such as the SiC [11], BN [12], SiO₂ [5], Al₂O₃ [13], and ZrO₂ [6] fibers. Among them, the sol–gel process provides an effective approach for ceramic-based nanofiber fabrication.

2.1. Fabrication Routes
2.1.1. Centrifugal Spinning

Centrifugal spinning is a method for the preparation of nanofibers that utilizes the centrifugal force generated by a high-speed rotation to convert the liquid into fibers. A schematic of typical centrifugal spinning equipment is displayed in Figure 1, which was employed to fabricate the fibers. The liquid is usually added to the container with a spinneret. For molten ceramic raw fibers, a high-temperature alloys container is usually used, maintaining its temperature over 1500 °C with a very high rotational speed, usually higher than 3000 rpm, to keep the raw ceramic material in a molten state [14]. When the centrifugal stress exceeds the surface tension of the liquid, the liquid will be injected from the spinneret to form several jets. The liquid flowing out of the sidewall will be stretched by the centrifugal force and air frictional force and reformed into fibers with a diameter of 1 μm or higher. To obtain nanofibers with an average diameter below 1 μm, liquid precursor centrifugal spinning is always employed as one of the most popular approaches for manufacturing nanofibers, such as ZrO₂ fibers [15], SiO₂ nanofibers [16], and Al₂O₃ nanofibers [17], etc. The schematic diagram of centrifugal spinning and corresponding equipment is shown in Figure 1.
2.1.2. Electrospinning

Besides centrifugal spinning, electrospinning is also a widely used method utilized for the fabrication of nanofibers [19,20]. Figures 2 and 3 show a schematic of an electrospinning process for manufacturing nanofibers [21,22]. Usually, a high-voltage electrical field is built between the nozzle and collector. Nanofibers formed at the nozzle owing to a much higher electrostatic force than the liquid jet’s surface tension. During the spinning, nanofibers are formed after the evaporation of the solvents. The ultrafine nanofibers are finally obtained on the collector, including organic nanofibers and Al₂O₃ nanofibers. Electrospinning is a typical method for nanofiber preparation, and it contains at least three typical steps: (1) preparation of a spinning solution consisting of precursors; (2) solution spinning under an electric field; and (3) calcination at high temperatures to obtain the inorganic nanofiber. Therefore, the advantages of electrospinning include structure and morphology control simply by adjusting the spinning parameters such as the composition of the spinning solution, electric field, and calcination conditions.
2.1.3. Solution Blow Spinning

Solution blow spinning is also one of the most effective fiber preparation approaches. It can produce a series of ceramic and polymer fibers with high efficiency and low cost [23,24]. Figure 4 displays a schematic diagram of a typical solution blow spinning, including a compressed air source, a collector, and a solution conveying device. During solution blow spinning, a solution is extruded through the inner nozzle and a high-speed gas flow is ejected through the outer nozzle, in which the solution forms a jet under the shear action of high-speed gas flow, which is further split and refined to form fibers. Similar to the electrospinning method, solution blow spinning also starts with the preparation of a spinning solution and ends with calcination, where the precursor firstly forms the raw fibers by blow spinning and finally calcination at high temperatures to form the ceramic fibers.

![Figure 3](image3.png)
*Figure 3. Schematic diagram of conjugate electrospinning (Reprinted with permission from Ref. [22]. 2017 Elsevier).*

![Figure 4](image4.png)
*Figure 4. Fabrication process of solution blow spinning (Reprinted with permission from Ref. [6]).*

Solution blow spinning is a simple procedure compared to electrospinning as shown in Figure 5, which makes it popular for the fabrication of nanofibers [25–28]. Compared to electrospinning, the solution blow spinning is high-voltage-free and it works with the high-speed gas flow as the driving force, thus it draws more attention for possessing a higher spinning efficiency.
2.1.4. Self-Assembly (Freeze-Drying)

The diameters of nanofibers are usually below 200 nm, and the lengths are several microns, which makes it hard to form the applicable materials. Therefore, self-assembly is an approach for combining nanofibers to build a novel morphology with adjustable structures. The mechanism of nanofiber self-assembly is the formation of hydrogels or a new nanofibric microstructure, which contains two routes: the liquid phase method and the solid phase method. The liquid phase method employs the liquid as a medium to dry a mixture of fiber precursor and liquid by removing the liquid phase to obtain hydrogels, such as the BN aerogel preparation process by Li et al. [30], which shows a preparation
process of BN nanoribbon aerogels by the self-assembly method. In addition, Si et al. [5] introduced a SiO$_2$ nanofiber aerogel shown in Figure 6, which was also fabricated by the self-assembly method. The SiO$_2$ nanofiber aerogel showed robust mechanical performance, such as twisting and excellent flexibility.

**Figure 6.** Fabrication process of SiO$_2$ nanofiber aerogel (CNFAs) (A) Schematic illustration of the fabrication of CNFAs. (B) XPS spectrum of CNFAs for all elements; a.u., arbitrary unit. (C) A CNFA heated by a butane blowtorch without any damage. (D) An optical image of CNFAs with diverse shapes. (E) An optical image showing a 20 cm$^3$ CNFA ($r = 0.15$ mg·cm$^{-3}$) standing on the tip of a feather. (F–H) The microscopic structure of CNFAs at different magnifications demonstrates the hierarchical nanofibrous cellular architecture. (I) STEM-EDS images of a single nanofiber with corresponding elemental mapping images of Si, O, Al, and B, respectively. (J) Schematic showing the three levels of a hierarchy of the relevant structures. (Reprinted with permission from Ref. [5]).

2.1.5. Other Routes

Except for the routes mentioned above, there are some other routes with the sol–gel method for the production of the nanofibers, such as the polymer conversion method, which is a method for preparing high-temperature resistant nanofibers from Si-, N-contained polymer, etc [31]. Clearly, it can be seen that there are differences among the above-mentioned method. The differences are summarized in Table 1 by Jia [1].
Table 1. Comparison of the main method for nanofiber preparation [1] (Adapted with permission from Ref. [1]. 2022 Donghua University).

<table>
<thead>
<tr>
<th>Methods</th>
<th>Material Types</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Fiber Diameter</th>
<th>Industrialization Prospect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Melt</td>
<td>High efficiency</td>
<td>Relatively poor flexibility</td>
<td>&gt; 1μm</td>
<td>High</td>
</tr>
<tr>
<td>Centrifugal spinning</td>
<td>Solution</td>
<td>High efficiency; broad material choice</td>
<td>Removal of polymer</td>
<td>Tens of nanometers to a few microns</td>
<td>Relatively high</td>
</tr>
<tr>
<td></td>
<td>Sol</td>
<td>High efficiency; high yield; polymer free</td>
<td>Uniform diameter</td>
<td>Hundreds of nanometers to tens of microns</td>
<td>Relatively high</td>
</tr>
<tr>
<td></td>
<td>Solution</td>
<td>Small and uniform diameter; diverse compositions and morphologies</td>
<td>Low efficiency; high voltage; removal of polymer</td>
<td>Tens of nanometers to a few microns</td>
<td>Relatively low</td>
</tr>
<tr>
<td></td>
<td>Sol</td>
<td>High yield; polymer free</td>
<td>Nonuniform diameter; high voltage</td>
<td>Tens of nanometers to a few microns</td>
<td>Relatively low</td>
</tr>
<tr>
<td></td>
<td>Solution</td>
<td>Simple and safe process; high efficiency; diverse compositions and structures</td>
<td>Removal of polymers</td>
<td>Tens of nanometers to a few microns</td>
<td>Relatively high</td>
</tr>
<tr>
<td>Solution blow spinning</td>
<td>Solution</td>
<td>Ribbon structure</td>
<td>Limited material choice; low efficiency; removal of organic</td>
<td>Width: hundreds of nanometers to a few microns. Thickness: a few nanometers</td>
<td>Low</td>
</tr>
<tr>
<td>Self-assembly</td>
<td>Solution</td>
<td>Non-oxide component</td>
<td>Low efficiency; calcination in inert atmosphere</td>
<td>Tens of nanometers to a few microns</td>
<td>Relatively low</td>
</tr>
<tr>
<td>Polymer conversion</td>
<td>Solution</td>
<td>Non-oxide component</td>
<td>Low efficiency; calcination in inert atmosphere</td>
<td>Tens of nanometers to a few microns</td>
<td>Relatively low</td>
</tr>
</tbody>
</table>

2.2. Nanofibers

2.2.1. Oxide Nanofibers

Oxide nanofibers possess the qualities of high-temperature resistance, oxidation resistance, high mechanical strength, great electrical, thermal, and acoustic insulation, as well as chemical stability. Among them, SiO$_2$, Al$_2$O$_3$, Mullite, ZrO$_2$, ZnO, and TiO$_2$ are usually employed to fabricate the corresponding ceramic-based nanofibers.

(1) SiO$_2$ nanofibers

As the most common oxide fibers, SiO$_2$ fibers are widely utilized in fields such as terrarium, electromagnetic transmission, and thermal insulation. The SiO$_2$ nanofiber is mainly employed as efficient thermal insulation at high temperatures. Therefore, most researchers are focusing on improving the thermal insulation performance of the SiO$_2$ nanofibers in a wide temperature range.

Si et al. [5] fabricated a SiO$_2$ nanofiber with an average diameter of 206 nm by a sol–gel electrospinning method. SiO$_2$ nanofiber aerogel with a mixed structure of layer-nanofibers-layer was further prepared by a fibrous freeze-shaping method using the flexible SiO$_2$ nanofibers as building blocks. Wang et al. [32] prepared flexible SiO$_2$ nanofibers with an average diameter of 162 nm by the sol–gel electrospinning method. The flexible SiO$_2$ nanofibers were used to construct a super elasticity biomimetic SiO$_2$ nanofibrous aerogel. Wang et al. [33] further obtained a ZrO$_2$/SiO$_2$ fiber membrane possessing a prominent removal efficiency of 85% and excellent adsorption amount of 43.8 mg·P·g$^{-1}$ in 30 min toward phosphates by modifying SiO$_2$ nanofibers with ZrO$_2$. Mi et al. [34] obtained 3D SiO$_2$ nanofibers with a low bulk density of 16 mg·cm$^{-3}$ and a high specific surface area of 6.5
m²·g⁻¹ by the sol–gel self-assembly and electrospinning method. The deposition and growth behavior of the 3D fibers were studied. The results indicated that the electrostatic repulsion among fibers caused a loose packing of fibers, and the rapid solidification of the fibers contributed to maintaining the 3D structure. Mao et al. [35] prepared SiO₂ nanofiber membranes by the combination of electrospinning and sol–gel methods, which possessed excellent flexibility of 0.0156 g·cm⁻¹, a tensile strength of 5.5 MPa, a thermal stability up to 1000 °C, and a high infiltration efficiency. Huang et al. [36] developed SiO₂ nanofibers by a combination of electrospinning and sol–gel methods, which possessed an ultralow density of 7.9–37 mg·cm⁻³, excellent resilient compressibility of 0.75 MPa at −85% strain, and a corresponding elastic modulus of 0.72 MPa. Yan et al. [21] employed sol–gel electrospinning to synthesize SiO₂ nanofibers films with a silk-like softness of < 31 mN, a low density of < 0.36 g·cm⁻³, and robust fire resistance of 1000 °C, which displayed large electrolyte uptakes of > 900% and high thermal insulation performance, enhancing the rate capability and safety of lithium batteries. Lu et al. [29] utilized a high-pressure gas spinning method to fabricate nanofibers/nanotubes with an individual setup of a throughput of 10 g·s⁻¹. In addition, a mechanism for the extrusion method was proposed based on flow mechanics and the experimental results, as shown in Figure 7.

Figure 7. Fiber forming mechanism via high-pressure gas spinning. (A–C) show the particles’ track after they had moved for 0.005, 0.075 and 0.12 s, respectively. (D) Proposed mechanism to explain the formation of nanofibers in the extrusion spray spinning process. (i) Scanning electron micrographs of the PVP nanofiber (or droplet) collected at different locations from 3 to 90 cm away from the spray nozzle. The inset is a transmission electron micrograph of the PVP nanofibers collected 180 cm away from the spray nozzle. (ii) Schematic illustrations showing the development from the
original PVP droplets to PVP nanofibers. (Reprinted with permission from Ref. [29]. 2012 Royal Society of Chemistry).

Ren et al. [37] prepared SiO\textsubscript{2} nanotube fibers with wall thickness < 100 nm and outer diameters in the range of 300–500 nm by centrifugal jet spinning. By using the same technology, Ren et al. [38] further fabricated a series of SiO\textsubscript{2} micro-/nanofibers with hollow or porous internal structure, whose solid cross sections were 364 and 781 nm, and the hollow cross sections were 458 and 216 nm, respectively. Tepekiran et al. [16] produced SiO\textsubscript{2} nanofibers via centrifugal spinning and subsequent calcination. The SiO\textsubscript{2} nanofibers fabricated by calcinated the 15 wt.% TEOS/PVP sample showed the highest filtration performance, and the average fiber diameter was the lowest, around 521 ± 308 nm. The nanofibers showed an enhanced filtration efficiency of around 75.89%.

(2) Al\textsubscript{2}O\textsubscript{3} nanofibers

Similar to the SiO\textsubscript{2} fibers, the Al\textsubscript{2}O\textsubscript{3} fibers are also widely applied in the fields of electromagnetic transmission and thermal insulation, especially for thermal insulation at high temperatures over 1000 °C. The Al\textsubscript{2}O\textsubscript{3} nanofibers are developed to solve the problems of growth in thickness and increase in thermal conductivity during utilization.

Mahapatra et al. [13] synthesized ultra-fine α-Al\textsubscript{2}O\textsubscript{3} nanofibers by using a mixture of PVP/ethanol solution and aluminum acetate sol via the electrospinning technique. The results showed that pure and crystalline α-Al\textsubscript{2}O\textsubscript{3} nanofibers with a diameter range from 100–500 nm and BET surface area of 40 m\textsuperscript{2}\cdot g\textsuperscript{-1} were formed. Wang et al. [39] fabricated mesoporous alumina fibers via an electrospinning technique combined with a sol–gel method, which exhibited uniform mesopores with a diameter range from 130–200 nm and a BET specific surface area up to 264.1 m\textsuperscript{2}\cdot g\textsuperscript{-1}. By transferring the γ-Al\textsubscript{2}O\textsubscript{3} to α-Al\textsubscript{2}O\textsubscript{3} at 1000 °C, the mesopores disappeared with a grain growth. The γ-Al\textsubscript{2}O\textsubscript{3} showed a great adsorption to Congo red with a maximum adsorption capacity of 781.25 mg·g\textsuperscript{-1}. Wang et al. [40] further fabricated γ-Al\textsubscript{2}O\textsubscript{3} nanofiber membranes by the electrospinning method. The nanofibers possessed a high aspect ratio, small diameter of 230 nm, high tensile strength of 2.98 MPa, and thermal stability of ~900 °C. Furthermore, the membrane exhibited great filtration performance for diocetyl phthalate, with a filtration efficiency of 99.8% at a pressure drop of 239.12 Pa when the basis weight was 9.28 g·m\textsuperscript{-2}. Filtration efficiency over 99.97% could be achieved when the basis weight was 11.36 g·m\textsuperscript{-2}. Song et al. [41] prepared Al\textsubscript{2}O\textsubscript{3} nanofibers by the sol–gel electrospinning method with different polymer templates, such as polyvinyl alcohol, polyvinyl butyral, and polyvinyl pyrrolidone. Three kinds of γ-Al\textsubscript{2}O\textsubscript{3} nanofibers were obtained and they exhibited completely different properties such as continuous structure, densification degrees, crystallization temperatures, grain sizes, tensile strength, and elastic modulus. Li et al. [42] obtained flexible Al\textsubscript{2}O\textsubscript{3} nanofiber mats by combing the sol–gel method with the solution-blowing process and a subsequent thermal treatment process. The as-spun nanofibers were formed after the solvent evaporation and drawing of the gas flow, and converted into γ- or α-Al\textsubscript{2}O\textsubscript{3} under a treatment in air at 900–1000 °C. The diameter range 2–5 μm and influenced by the spinning parameters, such as gel viscosity and high-pressure gas flow. Sedaghat et al. [17] manufactured an Al\textsubscript{2}O\textsubscript{3} nanofibers mat by a sol–gel spinning method using a self-laboratory designed centrifugal spinneret. It was found that θ-Al\textsubscript{2}O\textsubscript{3} was the main phase below 800 °C, which was transformed to α-Al\textsubscript{2}O\textsubscript{3} at 1000–1200 °C with an optimum silica percent of 4 wt.%. The wet was constructed by the nanofibers constituting a network with pore diameter ranges from 100 nm to 10 μm. When the silica content was lower than 10 wt.%, the fiber diameter had no effect. However, the grain size decreased from 200 nm to 100 nm or lower when the silica content was increased. Akia et al. [43] fabricated aluminum iso-propoxide and PE fine composite fibers utilizing the response surface methodology. The γ- and α-Al\textsubscript{2}O\textsubscript{3} nanofibers showed a diameter of 304 nm, while the γ-Al\textsubscript{2}O\textsubscript{3} nanofibers possessed a mesoporous structure with a BET surface area of 261 m\textsuperscript{2}\cdot g\textsuperscript{-1}.
(3) Mullite nanofibers

Mullite is a stable phase composed of SiO₂ and Al₂O₃ with an Al₂O₃ content of 72–78 wt.%, which possesses better coarsening resistance as compared to the single component of SiO₂ or Al₂O₃. Therefore, the mullite nanofibers are also widely applied as alternatives to SiO₂ and Al₂O₃, especially for thermal insulation for long-time service at high temperatures.

Liu et al. [44] prepared mullite-based nanofibrous aerogels via the gel-casting and freeze-drying methods with a series of different mullite of SiO₂:Al₂O₃ = 3:2–0, as shown in Figure 8. All the mullite nanofibrous possessed minor pores on the surface. They further overlapped to form nanofiber aerogel with multilevel porous structure, ultralow density of 34.64–48.89 mg·cm⁻³, low thermal conductivity of 0.03274–0.04317 W·m⁻¹·K⁻¹, and great physical and mechanical properties. Zadeh et al. [45] synthesized 3Al₂O₃·2SiO₂ nanofibers by combining the sol–gel and electrospinning methods with a mixture sol of aluminum isopropoxide, hydrated aluminum nitrate, and tetraethylorthosilicate. The optimal amount of PVB in the polymeric electrospinning solutions ranged from 4–6 wt.%, and the obtained mullite nanofibers were pure, smooth, and uniform, with a diameter of 85–130 nm. Song et al. [46] prepared flexible mullite nanofibers by an electrospinning method through the conventional diphasic mullite sol–gel route. The precursor sol was prepared by mixing aluminum acetate, colloidal silica, and the polyvinyl pyrrolidone. The mullite nanofiber was obtained after calcining at 1000 °C with an optimum Al/Si molar ratio of 2.98 and an elastic modulus of 25.18 ± 1.29 GPa. Xian et al. [47] fabricated mullite nanofibrous aerogels via the freeze-casting method by controlling the growth of ice crystals to adjust microstructure. The aerogel with high agarose content exhibited a relatively high compressive strength of 252.41 kPa owing to a high density and uniform porous structure. Song et al. [22] prepared continuous mullite nanofibers by the conjugate electrospinning technique combined with the sol–gel method by using the aluminum acetate stabilized with boric acid and tetraethyl orthosilicate. The obtained nanofibers showed an elastic modulus of 12.27 ± 1.77 GPa, and a tensile strength of 32.21 ± 3.73 MPa for the aligned mullite nanofiber bundle was obtained. Costa et al. [48] produced submicrometric mullite fibers via the solution blow spinning method. The mullite fibers were crack-free, possessed a diameter of 800 nm, and can be fabricated into fibrous mats showing a high surface area of 24 m²·g⁻¹.

![Figure 8. The fabrication process of the mullite-based nanofibrous aerogel (Reprinted with permission from Ref. [44]. 2018 Elsevier).](image-url)
ZrO$_2$ nanofibers

Ruiz et al. [49] used electrospinning for the preparation of PVP–zirconium acetate nanofibers in non-woven cloths. The ZrO$_2$ nanofibers showed a high aspect ratio and a thin thickness of 200 nm. Chen et al. [50] prepared ZrO$_2$ nanofiber membranes by electrospinning combined with the sol–gel methods. By incorporating yttrium oxide, the as-prepared ZrO$_2$ nanofiber membranes can be changed from extremely fragile to robust and offer greater flexibility for further application. Wang et al. [51] produced a resilient and heat-resisting yttria-stabilized ZrO$_2$ nanofiber sponge by a scalable solution blow spinning process. The porous 3D sponge showed a low density of 20 mg·cm$^{-3}$, and 99.4% filtration efficiency for aerosol particles (20–600 nm) with a low-pressure drop of only 57 Pa when the airflow velocity was 4.8 cm·s$^{-1}$. In addition, the sponge maintained a high filtration efficiency of 99.97% for PM 0.3–2.5 in an airflow velocity of 10 cm·s$^{-1}$. Wang et al. [6] fabricated a superfine ZrO$_2$ nanofiber ceramic aerogel with densities varying from 8 to 40 mg·cm$^{-3}$, which exhibited a maximum of 29.6 mJ·cm$^{-3}$ in energy density at 50% strain at a compression of 20%. The aerogel exhibited excellent resilience with residual strains of only ~1% at 800 °C after 10 cycles of 10% compression strain and good recoverability after compression at ~1300 °C.

Other oxide nanofibers SiO$_2$, Al$_2$O$_3$, and mullite are three of the main materials that are focused on the field of thermal insulation. There are other oxide nanofibers for other applications, such as nanofibers of ZnO [52–56], TiO$_2$ [57–65], CeO$_2$ [66], and CuO [67], etc.

2.2.2. Carbide Nanofiber

Carbide nanofibers are also widely employed as materials for thermal insulation, such as SiC, SiCN, and ZrC. Among them, SiC is the most investigated nanofiber. Owing to the covalent Si–C bond in SiC, SiC nanofiber displays excellent chemical stability and high mechanical resistivity below 1500 °C. Moreover, the performance of oxide high-temperature resistance could be further improved by doping or coating.

Su et al. [11] fabricated SiC nanowire aerogels consisting of a large number of interwoven 3C-SiC nanowires by chemical vapor deposition, which possessed an ultra-low density of 5 mg·cm$^{-3}$, a large strain recoverable compressibility over 70%, a low thermal conductivity of 0.026 W·m$^{-1}$·K$^{-1}$, and high organic solvent absorption properties of 130–237 g·g$^{-1}$. An et al. [68] synthesized a SiC nanofiber aerogel by rapidly stirring, freeze-drying, and applying a high-temperature treatment based on the fine SiC fibers prepared by electrospinning. The aerogel exhibited a low density of 0.039–0.041 g·cm$^{-3}$, and a low thermal conductivity of 0.025–0.031 W·m$^{-1}$·K$^{-1}$ for excellent thermal insulation. Liu et al. [69] employed the PMMA as a sacrificial template and co-axial electrostatic spinning to prepare N-doped hollow SiC fiber mats, as shown in Figure 9. The mats possessed a cavity wall thickness of approximately 1.5 μm, a low density of 0.218 g·cm$^{-3}$, and low thermal conductivity of 0.039 W·m$^{-1}$·K$^{-1}$. Li et al. [70] prepared micro-scale SiC nanofiber mats with great thermal stability and semi-conductivity by blowing off an oil-in-water (O/W) precursor, which was followed by an emulsification process, thermal curing, and high-temperature calcination.
Wang et al. [71] used electrospinning technology to obtain ultrafine ZrO2/SiC fibers. By pyrolysis at different temperatures, the fibers possessed a radial gradient composition and high-temperature stability over 1800 °C, as shown in Figure 10. Wu et al. [72] obtained a hydrophobic SiOC nanofiber membrane without any modification by the pyrolysis reaction of electrospun polycarbusilane nanofibers, as displayed in Figure 11. The nanofibers exhibited consistent hydrophobicity and strong mechanical properties throughout the pH and high temperature, as displayed in Figure 4. To prepare SiOC fibers with homogeneous morphology, the electrostatic spinning of a solution containing two (MK and H44) methyl silicones was employed. The effect of the processing process on the fibers was investigated by Guo et al. [73]. The results indicated that the introduction of 20 vol% N, N-dimethylformamide (DMF) was able to decrease the diameter of the as-spun fibers from 2.72 ± 0.12 μm to 1.65 ± 0.09 μm. For the H44/DMF system, the diameter of the spun fiber obtained by adding 50 vol% chloroform was 1.61 ± 0.16 μm. Both the pyrolyzed MK and H44-derived SiOC fibers have a uniform, defect-free morphology, small average diameter, and narrow size distribution.

Dong et al. [74] prepared a SiOC nanofiber aerogel via electrospinning assembly by the gel-casting and freeze-drying method, as exhibited in Figure 10. The aerogel possessed a low density of 46.87–128.48 mg·cm⁻³, low thermal conductivity of 0.0302–0.0440 W·m⁻¹·K⁻¹, high compressive strength of 18–167 kPa, and high specific surface area of 12.48–34.87 m²·g⁻¹. SiCN nanowires with efficient electromagnetic wave absorption properties were prepared by electrostatic spinning and high-temperature annealing (in a nitrogen atmosphere) by Wang et al. [75], which exhibited ultra-flexibility under winding and bending. The nanowires had an optimal reflection loss (RL) of −53.1 dB, and an effective absorption broadband (EAB) of 5.6 GHz.

Figure 9. Fabrication procedure illustration of N-doped hollow SiC fibrous mats (Reprinted with permission from Ref. [69]. 2013 Royal Society of Chemistry).

Figure 10. The morphology of the electrospun SiOC fibers after being calcined at 1000 °C (a) the low resolution and (b) the high resolution; (c) the diameter distribution of the electrospun SiOC fibers after calcined at 1000 °C (Reprinted with permission from Ref. [71]. 2018 Elsevier).
2.2.3. Nitride Nanofiber

(1) BN nanofiber

Similar to carbon, BN possesses a hexagonal, cubic, or tubular structure, and exhibits high thermal oxidation resistance and high radiation absorption capacity owing to its strong structural atomic connections of the B-N bond. Moreover, BN exhibits high thermal conductivity and desired mechanical property, enabling their potential utilization as thermal mechanical structure.

Song et al. [76] manufactured a BN aerogel by a template-assisted approach of low-pressure chemical vapor deposition on graphene–carbon nanotubes at 900 °C. It possessed an ultralow density of 0.6 mg·cm\(^{-3}\), an ultrahigh specific surface area up to 1051 m\(^2\)·g\(^{-1}\), and high hydrophobicity, which resulted in excellent oil absorption of up to 160 times by weight. Xue et al. [12] prepared h-BN nanofibers by employing the B\(_2\)O\(_3\) in situ chemical vapor deposition on 3D-SiO\(_2\)/N-doped tubular graphitic cellular foams. The foam was built by the h-BN nanofibers and possessed an interconnective nanotubular architecture. The foam featured with ultralight weight, thermal stability, high porosity of 98.5%, remarkable shape recovery for cycling compressed with 90% deformations, and excellent high-capacity adsorption–separation for oil/water systems. Li et al. [30] built a BN nanofiber aerogel with excellent temperature-invariant super-flexibility by a melamine diborane precursor. As exhibited in Figure 12, the aerogel was assembled by hydrogen bonding and possessed outstanding compressing/bending/twisting elasticity, cutting resistance, recoverable properties, and excellent mechanical super-flexibility over a wide temperature range of –196–1000 °C.
Figure 12. BN nanofibers: (a,b) SEM images, (c–e) TEM images, (f) an AFM image of BN nanoribbon aerogel, (g) STEM and element mappings of single BN nanoribbon, and (h) nitrogen adsorption–desorption isotherms of BN nanoribbon aerogels. Inset in (a), a BN nanoribbon aerogel monolith was placed on a flower. Inset in (b), the contact angle of BN aerogel. Inset in (d), the corresponding electron diffraction pattern. Inset in (h), the corresponding pore size distribution curve. (Reprinted with permission from Ref. [30], 2019 Wiley-VCH Verlag GmbH & Co. KGaA.)

(2) Si₃N₄ nanofiber

Si₃N₄ is another nitride ceramic that is widely investigated for thermal insulation and electromagnetic wave shielding, etc. Su et al. [77] produced ultralight α-Si₃N₄ nanobelt aerogels with density ranges from 1.8–9.6 mg·cm⁻³. The nanobelt aerogels owned resilient compressibility of a recoverable strain of 40–80%, great fire resistance at 1200 °C, excellent thermal insulation with a low thermal conductivity of 0.029 W·m⁻¹·K⁻¹, electronic wave transparency of a dielectric constant of 1–1.04, and a dielectric loss of 0.001–0.004. Huo et al. [78] fabricated 3D Si₃N₄ nanofiber-knitted ceramic foams via in situ reactive synthesis derived from silicon foams. The foams consisted of 3D nanofibers with a diameter of 15–100 nm. Zhang et al. [79] prepared Si₃N₄ nanowires via the vapor–solid process. The diameters of the nanowires ranged from 20–40 nm, and they had a specific surface area of 50.47 m²·g⁻¹, showing their promising applications in filtration, thermal insulation, and catalyst supports.

(3) Other nitride nanofibers

Except for the BN and Si₃N₄, some other important nitrides are valued for their excellent mechanical property and chemical stability, such as the GaN [80] used for the third semiconductor and AlN.

3. Materials Prepared by the Nanofibers and Their Thermal Management Applications

Ceramic-based nanofiber materials draw significant attention for thermal insulation applications owing to their low density, low thermal conductivity, high temperature resistance, good chemical stability, and good flexibility. Therefore, research on its application, especially at high temperatures, has been the focus in recent years.

To achieve high elasticity, Si et al. [5] prepared ceramic nanofiber aerogels (CNFAs) with superelastic layered structures by combining silica nanofibers with an aluminum-borosilicate matrix. Owing to their ultra-low density, fast recovery at 80% strain, zero Poisson’s ratio, and temperature invariant super-relaxation at 1100 °C, the CNFAs have
been used in insulation, catalysis, adsorption, energy, and acoustics, etc. They open up a wide range of technological implications.

The application of ultralight and porous nanostructures has been considerably limited by their brittleness. Wang et al. [6] prepared ceramic sponges consisting of a large number of twisted ceramic nanofibers based on oxide ceramics by a cost-effective blow-spinning technique. These ceramic sponges exhibited ultra-low density, high elasticity, and energy absorption, providing new insights into the design of porous cell structures for high-temperature applications.

Jia et al. [3] developed an anisotropic layered SiO$_2$-Al$_2$O$_3$ composite ceramic (SAC) sponge using a facile sol–gel solution blow spinning technique, which successfully solved the problem of the complicated preparation process of ceramic sponge materials. This sponge exhibited temperature invariant compression elasticity from $-196$ to $1000^\circ$C, good thermal conductivity of 0.034 W·m$^{-1}$·K$^{-1}$, and a density as low as 10 mg·cm$^{-3}$. The excellent properties are promising in the field of heat insulation and sound absorption.

Su et al. [11] reported highly porous 3D silicon carbide nanowire aerogels (NWAs) as shown in Figure 13. The NWAs had ultra-low density (5 mg·cm$^{-3}$), high porosity (99.8%), and good heat resistance properties (0.026 W·m$^{-1}$·K$^{-1}$ at room temperature in N$_2$), etc. These excellent properties make the NWAs promising in the field of fireproof materials and high-temperature insulation.

The creation of 3D nano aerogels (NFAs) is challenging. Si et al. [4] combined electrostatic spinning techniques and fiber freezing to prepare superelastic, layered cellular structured NFAs. The method enables the assembly of essentially layer-deposited electrostatic spun nanofibers into elastic aerogels with tunable density and shape. The NFAs exhibited a density of $>0.12$ mg·cm$^{-3}$. The bionic silica nanofiber (SNF) aerogel synthesized by Wang et al. [32] exhibited ultra-low density ($>0.25$ mg·cm$^{-3}$) and temperature invariant superelasticity up to 1100°C.

Liu et al. [78] used co-axial electrostatic spinning to prepare nitrogen-doped hollow silicon carbide fiber mats, in which PMMA was used as a sacrificial template to stabilize and pyrolyze the PCS/PMMA precursor. The cavity wall thickness of the hollow fiber was approximately 1.5 μm, while the mats possessed low density (0.218 g·cm$^{-3}$), high thermal conductivity (0.039 W·m$^{-1}$·K$^{-1}$), good flexibility and thermal stability. The properties of the mats suggest promising application as high-temperature thermal insulators. Dou et al. [81] synthesized a layered cellular structured silica nanofiber aerogel with adjustable density below 10 mg·cm$^{-3}$, excellent thermal insulation property with thermal conductivity of 0.029 W·m$^{-1}$·K$^{-1}$, and ultra-low dielectric constant due to the high porosity of NBAs. The
aerogels showed excellent refractoriness and high-temperature resistance, as exhibited in Figure 14.

Figure 14. (a) Fresh flower protected by HNA3 with a thickness of 2 cm under the heating of a butane blowtorch for 10 min. (b) Illustration of the measurement setup using a butane blowtorch. (c) Infrared thermal image of the front side subjected to the butane blowtorch flame. (d) Infrared images of the back side during the 30 min heating process: (d1) 30 s, (d2) 10 min, (d3) 20 min, and (d4) 30 min. (e) The time-dependent temperature profile of the center point on the backside. (f) Photograph of the front side after 30 min fire resistance test. (g) SEM of the front side after 30 min fire resistance test (Reprinted with permission from Ref. [81], 2019 American Chemical Society).

Su et al. [82] proposed the use of directional freeze casting and heat treatment to prepare SiC@SiO$_2$ nanowire aerogels with macroscopic pores to reduce the insulation (as exhibited in Figure 15). These aerogels have ultra-low thermal conductivity 14 mW·m$^{-1}$·K$^{-1}$ and excellent thermochemical stability (even at 1200 °C under butane blow gun), which are rational thermal insulation materials under extreme conditions. The new generation of elastomeric ceramic aerogels (CAGs) is distinguished in the field of thermal insulation by solving the problem of extreme conditions, where insulation materials need to be resistant to sharp thermal shocks and prolonged exposure to high temperatures [83]. In addition, Hu et al. [84] summarized the present researched thermal insulation materials utilized over 800 °C, in which the high-efficiency thermal insulation is almost built by the sol–gel routes as nanoparticle aerogels and nanofibers aerogels. They showed excellent thermal insulation performance with low thermal conductivities, as listed in Table 2. As has been mentioned above, ceramic-based nanofiber materials exhibit an excellent thermal insulation effect, especially at a relatively wide temperature range from negative up to 1000 °C, which indicates a direction to the development the more efficient thermal insulation materials applied in the conditions with higher temperature over 1500 °C, wider temperature range, or strong radiation environments.
Chemistry 2022, 4

Figure 15. Thermal superinsulation performance of the AH-SSCSNWA. Thermal conducting behavior of the AH-SSCSNWA in the (A) axial and (B) radial directions, respectively, showing the anisotropic heat transfer behavior in different directions. (C) The thermal conductivities of the AH-SSCSNWA in axial and radial directions. (D) A schematic illustration showing the mechanism to achieve thermal superinsulation. (Reprinted with permission from Ref. [82]).

Table 2. Physical properties of some high-temperature nanofibers aerogel.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (mg·cm(^{-1}))</th>
<th>Thermal Conductivity (W·m(^{-1})·K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2) nanofibrous [84]</td>
<td>0.2–17</td>
<td>0.0223</td>
</tr>
<tr>
<td>Al(_2)O(_3), SiO(_2) nanofiber [44]</td>
<td>34.64–48.89</td>
<td>0.03274–0.04317</td>
</tr>
<tr>
<td>Al(_2)O(_3), ZrO(_2) nanofibrous [84]</td>
<td>-</td>
<td>0.0322 at 1300 °C</td>
</tr>
<tr>
<td>Al(_2)O(_3)-SiO(_2) micron fibers and nanoparticles [84]</td>
<td>0.36</td>
<td>0.082 at 1200 °C</td>
</tr>
<tr>
<td>BN nanobelts [30]</td>
<td>15.5</td>
<td>0.0346 ± 0.0015</td>
</tr>
<tr>
<td>Si(_3)N(_4) nanobelts [77]</td>
<td>1.8–9.6</td>
<td>0.029</td>
</tr>
<tr>
<td>SiC Nanowires [84]</td>
<td>11</td>
<td>0.025</td>
</tr>
</tbody>
</table>

High-temperature insulation is widely used in various fields, such as aerospace, construction, and other fields.

Wang [85] studied a sapphire optical fiber high-temperature sensor sealed in an alumina ceramic tube–ceramic sleeve structure. The sensor has a measurable range of 25–1550 °C, good stability, high-temperature detection accuracy, and a very broad application prospect in high-temperature fields such as aircraft engines and gas turbines. Solid oxide fuel cells (SOFCs) are the most flexible, cleanest, and most efficient chemical–electrical energy conversion systems among all types of fuel cells. Chen [86] avoided the disadvantages of the fuel by surface modification of electrocatalytic activity consisting of conformal PNM films and dissolved PrOx nanoparticles, which enhanced hybrid catalyst coatings. He [87] explored a new method of membrane-based propane POX, in which propane reacts with permeate oxygen to syngas in the presence of the Ru-Ni catalyst (Figure 16). The membrane reactors are superior to conventional reactors in terms of safety.
and syngas concentration, so they have great application prospects as pre-reformers for solid oxide fuel.

Figure 16. Illustration of POX membrane reactor (Reprinted with permission from Ref. [87]. 2018 Elsevier).

Gao [88] provides a perspective on solid oxide fuel cells (SOFCs) operating at low temperatures (LT) (400–650 °C). The LT-SOFCs exhibited good battery performance at low temperatures, offer potential advantages in traditional SOFC applications, and may be suitable for new portable and transport power applications. Higher-temperature SOFCs are currently being commercialized. Yang [89] focused on the research of lightweight layered silicon pore gradient ceramic aerogel foam. The high porosity and large pore gradient of the aerogel endowed it with excellent thermal properties. Meanwhile, the hydrophobic PGA foams have mechanical stability and fire resistance in humid environments, as shown in Figure 17, which plays an important role in building materials.

Cheng [90] prepared a new lightweight needle-like carbon fiber felt/phenolic resin (NCF-PR) aerogel composite. The aerogel composite had a unique bird’s nest structure, which provides excellent thermal insulation and ablation performance in the arc jet wind tunnel simulation environment, as exhibited in Figure 18. They showed great application potential in aerospace thermal insulation.

Figure 17. (a) Thermal conductivities of the series of PGA foams dependent on average pore size and porosity. (b) Thermal conductivity corresponding to different post annealing temperature and thermal conductivity before and after hydrophobicity treatment (Reprinted with permission from Ref. [89]. 2020 American Chemical Society).
Figure 18. Screenshot of sample NCF-PR1/4 during the ablation test in an arc-jet wind tunnel recorded by camera from 1 to 33 s (Reprinted with permission from Ref. [90]. 2017 Elsevier).

Jin [91] developed a clay aerogel with both hydrophobic and mechanical robustness. The aerogel exhibited ultra-low density, limiting oxygen index of up to 90%, and fire resistance at 1000 °C for ten minutes. Thus, it is a very promising material for construction and aerospace owing to its heat insulation and fire resistance. Nguyen [92] reported a family of triisocyanate aerogels formed by crosslinking amine-capped polyimide oligomers and triisocyanates. The backbone chemistry, chain length, and polymer concentration determine its low density, large surface area range, and high compression modulus. Due to its low cost, the aerogel can be widely used. In the case that its low temperature stability could be solved, the aerogel would attract more attention in aerospace application. Compared to traditional thermal management materials, the materials obtained from the sol–gel route possesses higher strength and stiffness by selecting appropriate silane precursors and polymer reinforcement. Randall [93] discussed some strategies to improve the strength and elasticity of silica aerogels in recent years, as listed in Figure 19, so that silica aerogels can be more suitable for future applications.

Figure 19. Current and proposed aerospace applications of aerogels, showing (a) Mars rover, (b) an inflatable decelerator concept for EDL applications, and (c) an EVA suit (Reprinted with permission from Ref. [93]. 2011 American Chemical Society).

4. Conclusions

Developments and applications of ceramic-based nanofiber materials in the last decade have been summarized in this review. The types of nanofibers including oxide, carbide, nitride, and other ceramic-based nanofibers, and their preparation methods, such as centrifugal spinning, electrospinning, solution blow spinning, and self-assembly, which have been employed for realizing the superfine nanofibers, are summarized. The development of fabrication methods has prompted the applications of the ceramic-based nanofibers in the fields of sound insulation, electromagnetic wave insulation, and thermal insulation. In particular, the ceramic-based nanofibers find specific applications in high-
temperature thermal insulation. Based on the above summarization, it can be concluded that the production of superfine ceramic-based nanofibers is the development direction for the high-performance thermal management materials, and the sol–gel route is the most efficient approach. There still exist some problems that will prevent it from rapid development and commercialization. Some tips to avoid or solve these problems for the development and application of the ceramic-based nanofibers are proposed:

1. Avoid the utilization of polymers to enhance the quality of nanofibers. Polymers result in fiber diameter reduction, formation of porous surface, and decrease in mechanical capacity. The way to eliminate this phenomenon is to enhance the solid content as much as possible and avoid polymer utilization.

2. Multiphase component nanofibers. For some single-component, ceramic-based nanofibers, their performance will decrease because of the nanometer effect. It is therefore necessary to obtain multiphase component nanofibers by adding some other components to improve their performance, such as the YSZ-Al₂O₃ nanofibers.

3. Improvement for efficient commercialization. The solution blow spinning possesses the highest efficiency to prepare nanofiber-based products, such as films and sponges, which ought to receive more research attention.

**Author Contributions:** J.Z. (Jing Zhang), J.Z. (Junxiong Zhang), Q.S., X.Y., X.M., and J.W. co-write the manuscript. J.Z. (Junxiong Zhang) and J.W. supervised and obtained funding for the project. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was funded by the Talent Introduction Project Foundation of Nantong University (135421615077); Large Instruments Open Foundation of Nantong University (KFJN2237); the National Natural Science Foundation of China (91963124), the Suzhou Municipal Science and Technology Bureau (SJC2021008); China Postdoctoral Science Foundation (2021M702665); and Natural Science Foundation of Shaanxi Province (2022JQ-482).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


93. 
No specific content available.