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# Ultralight and superelastic ceramic nanofibrous aerogels: a new vision of an ancient material

Yi-Tao Liu, Bin Ding *

*Innovation Center for Textile Science and Technology, Donghua University, Shanghai 200051, China*

Ceramics, a huge family of inorganic compounds including oxides, nitrides, carbides, silicates, aluminates, phosphates, etc., are among the most ancient materials whose service to mankind could date back to ~7000 years ago. Owing to strong covalent or ionic bonds linking the constituent atoms, ceramics possess good mechanical strength and heat resistance, and have long been used as the structural components particularly at high temperatures. Since 1930's, the concept of functional ceramics has been introduced, aiming to exploit the unique electronic, magnetic, optical, chemical, and biological functionalities of some specific ceramics. Despite the brilliant history of this century-old material, it should be noted that all ceramics are heavy and brittle by their very nature, and these inherent drawbacks severely limit their applications in frontier domains such as hypersonic vehicles, wearable electronics, and flexible batteries, where lightweight and elastic ceramic components withstandable to harsh serving environments (high-frequency vibration or high-intensity bending) are highly desirable.

Aerogels, on the other hand, refer to an amazing class of highly porous, ultralight solids full of air as the dispersed phase, which was ranked as one of Top Ten Emerging Technologies in Chemistry 2022 by the International Union of Pure and Applied Chemistry (IUPAC). As early as 1931, Kistler [1] created the first ceramic aerogels composed of $SiO_2$ nanoparticles arranged in a pearl-necklace-like microstructure, which exhibited ultralow density and thermal conductivity, holding the potential as a candidate for lightweight superinsulation in aerospace. Since then, a series of other ceramic aerogels, including $TiO_2$, $ZrO_2$, $Al_2O_3$, etc., were developed for some down-to-earth applications, such as catalysis, drug delivery, and water purification. Unfortunately, these nanoparticle-constructed ceramic aerogels are still frustrated by high brittleness owing to weak particle–particle interactions, making their practical applications lagging far behind the fundamental researches. The ability to transform ceramics from brittle to flexible and even elastic remains a formidable yet fascinating challenge.

Compared to zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanofibers are characteristic of high aspect ratio and good structural continuity, capable of tolerating large bending deformation along the axial direction, so they can endow ceramics with excellent flexibility. Through intentional assembly of flexible ceramic nanofibers, researchers have created aerogel-like, highly porous three-dimensional (3D) frameworks (porosity >99% in most cases). More importantly, the 1D nanofibrous building blocks are easily intertwined through physical or chemical bonding, so their 3D assemblies possess sufficient and stable space to dissipate the external stress through large and reversible deformation, leading to superelasticity. The resulting ultralight and superelastic 3D ceramic frameworks, generally called ceramic nanofibrous aerogels (CNFAs), represent an important advance by bringing the ancient ceramic material to many cutting-edge fields, as shown in Fig. 1a. In this sense, an introduction to the origin and development of CNFAs, focusing on different structural engineering strategies, is meaningful to a better understanding of their structure–property relationships.

The door to nanofibrous aerogels (NFAs) was opened by Ding and co-workers [2] in 2014, who reported the earliest, cellular-structured NFAs by ice-crystal-assisted assembly of $SiO_2$ and polyacrylonitrile (PAN) nanofibers. The density of the $SiO_2$/PAN NFAs was as low as 0.12 mg $cm^{-3}$, which set a new record for the lightest solid [3]. Subsequently, the same group [4] fabricated the first all-ceramic NFAs, involving the dispersion of flexible $SiO_2$ nanofibers in water under homogenization, the ice-crystal-assisted assembly into a cellular structure under freezing, and the formation of aerogels under freeze-drying (Fig. 1b). In contrast to our traditional impression of $SiO_2$, such as glass or quartz, the $SiO_2$ NFAs had an ultralow density of 0.15 mg $cm^{-3}$, corresponding to a porosity up to 99.993%, which made them even lighter than a feather. More strikingly, the $SiO_2$ NFAs broke the limitations of brittleness and stiffness set by Mother Nature on ceramics, and could be repeatedly compressed at a large strain of 60% with tiny plastic deformation (8% after 100 cycles and 12% after 500 cycles). The ultralight and superelastic properties, combined with ultralow thermal conductivity (0.025 W $m^{-1}$ $K^{-1}$ at ambient temperature and pressure, even close to that of standing air) and good heat resistance, endowed the $SiO_2$ NFAs with great possibilities to effectively combat the thermal shock as a superinsulation material, an obvious merit over the nanoparticle-constructed $SiO_2$ aerogels.

$TiO_2$ is a representative functional ceramic widely used in paint, food additive, sunscreen, as well as photo- and electrocatalysis owing to its extraordinary optical and electronic properties. However, it exists generally in the powder form of micro- or

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* Corresponding author.
*E-mail address:* binding@dhu.edu.cn (B. Ding).

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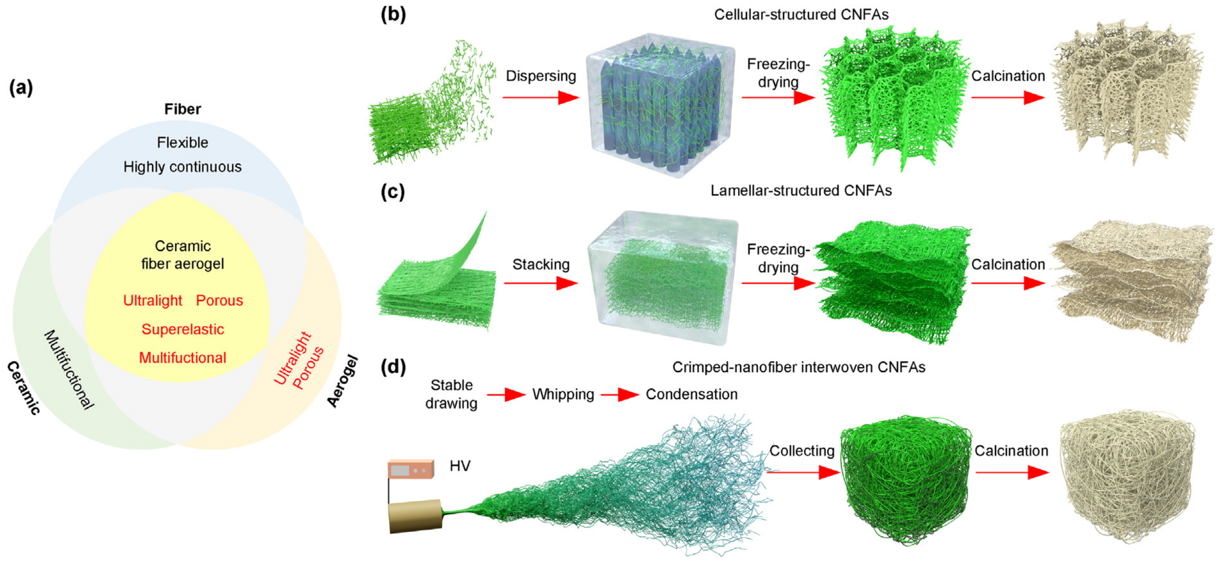

**Fig. 1.** (Color online) (a) The creation of ultralight and superelastic CNFAs through rational combination of the merits of "ceramic", "fiber", and "aerogel", and the schematic illustration of the fabrication process of (b) cellular-structured CNFAs, (c) lamellar-structured CNFAs, and (d) crimped-nanofiber interwoven CNFAs.

nanoparticles, and could be easily inhaled by the human body during production and usage, causing serious health hazards. As such, the European Union has officially announced the mixtures containing ≥1% $TiO_2$ micro- or nanoparticles as a Category-2 Carcinogen. As such, Liu and co-workers [5] transformed $TiO_2$ into NFAs by freeze-drying, which could withstand 100 compression cycles at a strain of 25% with only 4.8% plastic deformation. This invention provided an interesting idea of addressing the health issue faced by $TiO_2$ in the powder form. The electronic structure of the $TiO_2$ NFAs was further modulated by Li reduction, resulting in "black" $TiO_2$ NFAs with abundant oxygen vacancies whose conductivity was increased by 3 orders of magnitude. The conductive and superelastic $TiO_2$ NFAs represented a conceptually new class of self-supported electrocatalysts, delivering superior activity and long-term durability in a proof-of-concept, electrocatalytic $N_2$ reduction experiment. Moreover, the freeze-drying strategy was also effective on the construction of non-oxide CNFAs, e.g., hydrophobic and squeezable $Si_3N_4$ NFAs which were demonstrated to be a good choice of oil/water separation with high absorption capacity and good oil recovery ability [6].

Note that the above CNFAs were assembled from short-cut nanofibers randomly bound together by relatively few, point-to-point contacts in all directions, so they suffered from low compressive strength (generally <10 kPa). As such, researchers conceived anisotropic, lamellar-structured aerogels to enhance the interlayer compressive strength. For example, Zhang et al. [7] prepared lamellar $ZrO_2$–$Al_2O_3$ NFAs (90–100 mg $cm^{-3}$) through layer-by-layer stacking of electrospun nanofibrous membranes in a binder solution, followed by freeze-drying and high-temperature curing (Fig. 1c). Such a unique structural arrangement, comprising strongly face-to-face bound layers, ensured a compressive strength of more than 1100 kPa at a strain of 90%, combined with high fatigue resistance (1000 compression cycles at a strain of 60%). Based on a similar idea, Jia et al. [8] employed blow-spinning to obtain layer-stacked CNFAs (22.5 mg $cm^{-3}$), which exhibited a compressive strength of 13.5 kPa at a strain of 80%, and fatigue resistance of 600 compression cycles at a strain of 50%. Besides, Ren and co-workers [9] mixed aluminoborosilicate nanofibers and $SiO_2$ sol, and employed vacuum filtration to obtain $SiO_2$-filled, lamellar-structured CNFAs (50 mg $cm^{-3}$), delivering ~60 kPa compressive strength at a strain of 60% and 100-cycle fatigue resistance at a strain of 50%.

Despite superior compression resilience, the above CNFAs were cross-linked by using a binder to stabilize the highly porous structure because of the lack of intrinsic fiber–fiber interactions, leaving no room for tensile deformation. How to acquire stretchability remained an important task for CNFAs, since it was a prerequisite for many practical applications where the brittle fracture of the ceramic components was catastrophic. As such, Cheng et al. [10] proposed a new strategy of 3D reaction electrospinning, in which a rapid sol–gel reaction was enabled during the early stage of jet whipping, and the jet solidified at this stage to form a highly crimped fiber structure, as shown in Fig. 1d. By designing the vertical movement of the nozzle and collector, they interknitted the crimped nanofibers into CNFAs (e.g., mullite, $Al_2O_3$, $ZrO_2$). These CNFAs, totally distinct from the cellular- or lamellar-structured aerogels, were composed of crimped nanofibers that were randomly entangled and physically interlocked, capable of providing an effective means of dissipating the tensile stress through fiber slipping. As such, they could be stretched by a strain up to 100% without fracture, and withstand 1000 stretching cycles at a strain of 40%. The temperature-invariant stretchability, together with the potential for scalable production, made the CNFAs a lightweight, robust superinsulation material used in extreme environments, e.g., complex aerothermal environment faced by the hypersonic vehicles.

To further enhance the mechanical properties of CNFAs, Wu et al. [11] introduced a multiphase design to individual nanofibers, in which nanograins of mullite and $\alpha$-$Al_2O_3$ were uniformly embedded in a glass matrix of aluminosilicate. The nanograins acted as the reinforcing sites, while the surrounding glassy matrix offered sufficient stress-absorbing deformation, increasing the tensile strength of the ceramic nanofibers from 596 to 829 MPa. The resulting CNFAs showed enhanced mechanical strength as well as structural stability from deep-cryogenic (−196 °C) to ultrahigh temperature (1600 °C). By a similar nanograin–glass dual-phase design, Li et al. [12] prepared elasto-flexible, fatigue-tolerant, and heat-insulating CNFAs of, e.g., $ZrO_2$–$SiO_2$, $Al_2O_3$–$SiO_2$, etc. These CNFAs also displayed temperature-invariant superelasticity from cryogenic −196 to 1500 °C.

Other than the applications of superinsulation and sound absorption, the CNFAs could also be functionalized to extend the application fields by hybridization with a second component. For example, Zong et al. [13] reported CNFAs with hierarchically entangled reduced graphene oxide (rGO) networks through co-dispersion of $SiO_2$ nanofibers, GO nanosheets, and ascorbic acid in water, followed by freeze-drying and calcination to reduce GO. The resulting hybrid aerogels were composed of 1D $SiO_2$ nanofibers wrapped by 2D rGO nanosheets in the form of bridging, soldering, and jointing, and the sandwiched lamellar structure along the thickness direction enabled multi-interface reflection of the acoustic wave. As such, they exhibited significantly enhanced broadband noise absorbance with a noise reduction coefficient of 0.56 in the range of 63–6300 Hz, as well as temperature-invariant stability from −100 to 500 °C, a merit significantly over the traditional, polymer-based sound-absorbing material that could only be used in a narrow temperature range. In another case, Zhang et al. [14] fabricated bone-repairing hybrid aerogels consisting of interwoven tricalcium phosphate nanofibers and hydroxyapatite nanowires by freeze-drying, in which the former functioned as a regenerative component owing to their bone similarity together with excellent osteoconductive and osteoinductive properties, while the latter were responsible for constructing a highly interconnected network owing to their mechanical robustness. Note that the aerogel structure was particularly favorable for the surgical operation owing to their ability to be processed into different shapes and dimensions; moreover, they could be filled in a bone defect in a compressed state, and recover to the original state upon wetting to fill the bone cavity. Additionally, Dong et al. [15] developed carbon nanotubes (CNTs)@$SiO_2$ hybrid aerogels by mixing $SiO_2$ nanofibers and CNTs in water followed by freeze-drying, which were featured by vertically aligned vessels and porous walls enabling salt-resistant convection and diffusion of seawater. As such, a light absorbance of 98% and an evaporation rate of 1.50 $kg\ m^{-2}\ h^{-1}$ under 1-sun irradiation were achieved, making the CNTs@$SiO_2$ hybrid aerogels a promising candidate for the seawater desalination in an efficient and long-serve-life manner.

In summary, we present a brief overview on the structural engineering strategies of the ultralight and superelastic CNFAs, which have broken the stereotype of ceramics, and brought about numerous new opportunities to this ancient material. In the future, the CNFAs are destined to better and faster development, and two important directions are envisioned. First, the present CNFAs are mostly constructed from oxide ceramic nanofibers since the preparation of flexible non-oxide ceramic nanofibers is still a challenging task, which largely restricts their application range. Therefore, efforts need to be made to achieve technological breakthrough in the fabrication of non-oxide CNFAs. Second, the pore structure modulation of CNFAs is rather primitive currently, limiting their application performance to a large extent. Strategies for precisely controlling the pore structure and size are highly desirable, particularly in the fields of sound absorption, heat insulation, etc.

## Conflict of interest

The authors declare that they have no conflict of interest.

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Yi-Tao Liu received his B.S. degree (2003) from Harbin Institute of Technology, and M.S. (2006) and Ph.D. (2012) degrees from Tsinghua University. Then, he did post-doctoral research at the Department of Chemical Engineering and Department of Precision Instruments, Tsinghua University from 2012 to 2017. After working at the College of Materials Science and Engineering, Beijing University of Chemical Technology, he is now a professor at the Innovation Center for Textile Science and Technology, Donghua University. His research interest focuses on functional ceramic nanofibrous materials and their environmental and energy applications.

Bin Ding received his B.S. degree (1998) from Northeast Normal University, and M.S. degree (2003) from Chonbuk National University. After that, he earned his Ph.D. degree (2005) from Keio University. Currently, he is the dean of the Institute of Science and Technology, Donghua University. His research mainly focuses on flexible ceramic nanofibers, waterproof and breathable materials, filtration materials, oil/water separation materials, nanofibrous aerogels, etc.