

Freeze Casting for Assembling Bioinspired Structural Materials

Qunfeng Cheng, Chuanjin Huang, and Antoni P. Tomsia*

Nature is very successful in designing strong and tough, lightweight materials. Examples include seashells, bone, teeth, fish scales, wood, bamboo, silk, and many others. A distinctive feature of all these materials is that their properties are far superior to those of their constituent phases. Many of these natural materials are lamellar or layered in nature. With its “brick and mortar” structure, nacre is an example of a layered material that exhibits extraordinary physical properties. Finding inspiration in living organisms to create bioinspired materials is the subject of intensive research. Several processing techniques have been proposed to design materials mimicking natural materials, such as layer-by-layer deposition, self-assembly, electrophoretic deposition, hydrogel casting, doctor blading, and many others. Freeze casting, also known as ice-templating, is a technique that has received considerable attention in recent years to produce bioinspired bulk materials. Here, recent advances in the freeze-casting technique are reviewed for fabricating lamellar scaffolds by assembling different dimensional building blocks, including nanoparticles, polymer chains, nanofibers, and nanosheets. These lamellar scaffolds are often infiltrated by a second phase, typically a soft polymer matrix, a hard ceramic matrix, or a metal matrix. The unique architecture of the resultant bioinspired structural materials displays excellent mechanical properties. The challenges of the current research in using the freeze-casting technique to create materials large enough to be useful are also discussed, and the technique’s promise for fabricating high-performance nacre-inspired structural materials in the future is reviewed.

of the challenges of designing and making new materials have been addressed by nature over millions of years of evolution. By drawing inspiration from nature, numerous research groups are trying to mimic the architecture of natural materials and fabricate composites with unique properties.^[1] Nacre is one of the most studied natural structures because of its extraordinary physical properties, including exceptional strength and toughness. Nacre is made of 95 vol% of mineral calcium carbonate (aragonite platelets) bonded by 5 vol% of organic layers of chitin and proteins. The brick and mortar structure of nacre exhibits remarkable toughness, which is about 3000 times higher than that of pure calcium carbonate.^[2] Nacre’s high flaw tolerance and fracture toughness are due to its sophisticated micro-/nanoscale hierarchical architecture and abundant interfaces between mineral calcium carbonate and organic layers.^[3] The interfacial adhesion between the hard phase (aragonite) and soft phase (organic matrix) is highly optimized such that the limited interlayer shearing during fracture acts as a toughening mechanism. If instead of weak calcium carbonate, stronger and tougher building blocks

are chosen to mimic nacre, much better materials could be fabricated.^[4,5]

This challenge can be met through an understanding of the relationships between the architecture of natural materials and their mechanical response, spanning not simply the microstructure but the structural parameters from the atomic to macro length scales. The architecture and many of the properties of

1. Introduction

A major scientific challenge for the 21st century is the development of stronger and tougher (damage-tolerant) structural materials that ideally are lighter weight to support advances in strategic fields, from buildings to transportation to energy.^[1] How to make these new materials is not entirely clear. Some

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materials are determined to a large extent by the properties of their internal interfaces. Therefore, the translation of natural designs requires a deep understanding of the mechanical behavior of materials and interfaces in small volumes, down to the nanoscale. This area of research, mimicking natural materials, is enormous and in a rapid state of development.

Many processing techniques have been proposed to produce nacre-like and other bioinspired materials, such as layer-by-layer deposition,^[6,7] filtration,^[8–10] evaporation,^[11] electrophoretic deposition,^[12] hydrogel casting,^[13–15] doctor blading,^[16,17] slip casting,^[18] and many others. Most of these techniques are time-consuming and size-limiting processes, and not feasible for practical materials production. They are limited to making a few thick ($\approx 200\ \mu\text{m}$) ceramic layers that, due to their small size, are not yet suitable for structural applications and do not replicate distinctive features of natural materials. Thus far, the field has been largely unsuccessful in its quest to apply nature's secrets to engineering materials and design.

Corni et al.,^[19] in their comprehensive review of the techniques mentioned previously, stated that the most promising strategies for the production of nacre-like materials are freeze casting, hot-press-assisted slip casting, electrophoretic deposition, and the paper-making method. Of these, freeze casting and hot-press-assisted slip casting are probably the best-suited techniques to produce bulk materials with complex shapes and architectures that mimic nacre and exhibit outstanding properties.

Freezing colloidal particle suspensions is not a new phenomenon. The earliest publications on the topic date to 1926.^[20,21] However, the process did not receive much attention until 2006, when DeWille et al.^[22] published a seminal paper in *Science* describing the freeze-casting technique to make new materials. This resulted in the development of a new class of bioinspired, ultrahigh-toughness ceramic materials^[22,23] by controlled freezing of ceramic-based suspensions in water. The technique, a relatively inexpensive procedure, provides a means to mimic natural structural designs over several length scales. The freeze-casting technique has overcome many of the limitations of other conventional techniques described previously. The technique creates materials that exhibit a hierarchical architecture with interconnected porosity formed by aligned, thin, porous layers.

As several recent reviews describe the technique and applications for constructing nacre-like ceramic materials via freeze casting,^[24–27] only a brief description of the technique is provided here. We discuss recent progress in using the freeze-casting technique to assemble bioinspired structural materials with different building blocks and how to optimize the processing parameters of the freeze-casting technique. Finally, we provide a perspective and outlook for future directions of using the technique to fabricate novel materials.

2. Freeze Casting for Assembling Different Building Blocks

Freeze casting is a wet-processing technique that utilizes directional solidification of water-based (or other solvent) suspensions (ceramic, metal, or polymers), resulting in straightforward



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self-assembly of particles to form a highly porous bulk material. The technique is very flexible, inexpensive, and environmentally friendly. It can be extended to a wide range of materials combinations, utilizing different building blocks, including nanoparticles, polymer chains or nanofibers, and nanosheets, as shown in **Figure 1**. The freezing conditions are designed such that the growing ice has a lamellar microstructure and the particles concentrate in the space between the ice crystals to yield a layered, homogeneous scaffold whose architecture is a negative replica of the ice.^[22]

By controlling the freezing kinetics and the composition of the suspension, it is possible to tailor the architecture of the material at multiple length scales and replicate some of the microstructural features behind the unique mechanical response of a natural lamellar material like nacre. Various types of microstructures^[28] can be obtained depending on the powder, the freezing conditions, the solvent used, or the presence of additives. Several studies have established the relationship between the processing conditions (slurry concentration, freezing rate, and sintering) and the scaffold architectures (size and amount of porosity, wall thickness, interlamellar bridging, and roughness of internal surfaces^[29–39]). Faster freezing rates result in much finer microstructures. Additives that affect

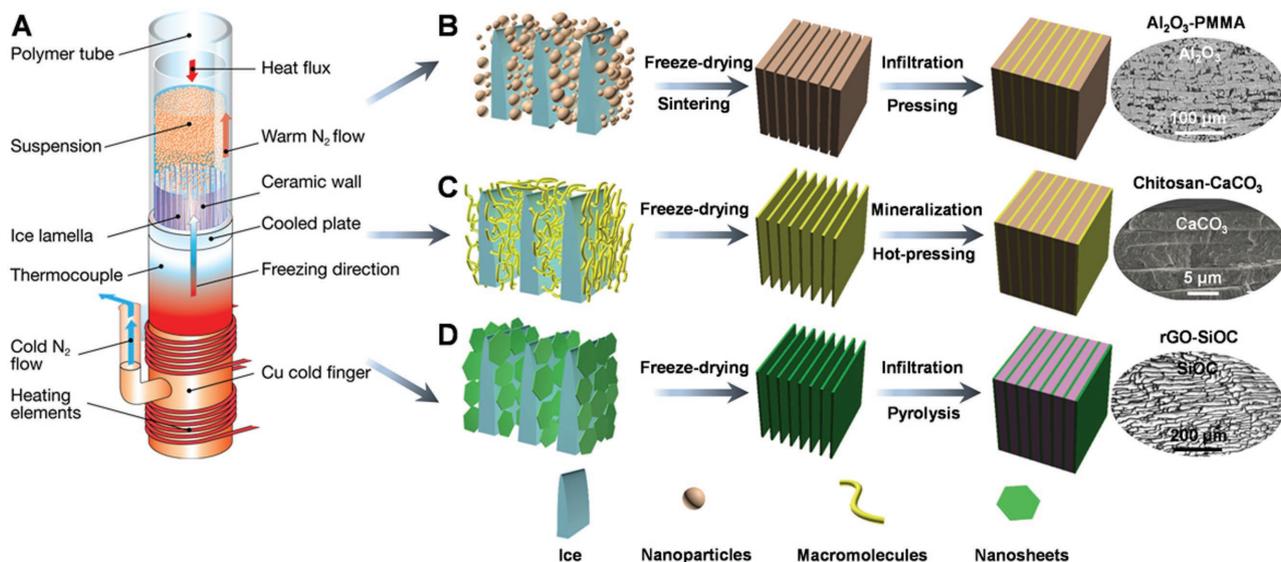


Figure 1. A) Schematic of the freeze-casting technique showing the resulting bioinspired nacre-like nanocomposites. As the ice grows, it expels the nanoparticles (B), macromolecules (C), and nanosheets (D) that accumulate in the space between ice crystals. A lamellar structure, where the pores are a direct replica of the ice crystals, is obtained. After sublimating the water (or other solvent), ceramic or metal scaffolds are thermally treated to sinter and consolidate the structure. A) Reproduced with permission.^[1] Copyright 2014, Nature Publishing Group. SEM images in Figure 1B: reproduced with permission.^[23] Copyright 2008; SEM images in Figure 1C: reproduced with permission.^[61] Copyright 2016, American Association for the Advancement of Science; SEM images in Figure 1D: reproduced with permission.^[49] Copyright 2017, Nature Publishing Group.

the physical parameters controlling the microstructure of the growing ice (such as the phase diagram of the solvent, degree of supercooling ahead of the freezing front, and the solid/water and the ice/solvent interfacial energies) can be used to modify the shape and internal roughness of the lamellae. For example, when water is used, the pore morphology is lamellar, while a solution of camphene and naphthalene–camphor creates dendritic channels. With *tert*-butyl alcohol, the channels are prismatic.

To obtain scaffolds with cellular or lamellar morphology, and with porosity oriented along the temperature gradient, faster cooling rates are required (1–25 °C min⁻¹) and higher solid contents (15–50 vol%), with those ranges depending on the material. It should be noted that there is a critical value for solid content^[40] or ice-front velocity above which particles will be entrapped randomly by the freezing front, resulting in the loss of the lamellar structure.^[39] The thermodynamics of freeze casting showing conditions for the particle rejection or entrapment have been described by Wegst et al.^[27] and Deville et al.^[41] The critical ice velocity for particle entrapment is inversely proportional to the particle radius.^[42] Thus, repelling small particles from the ice front is easier than repelling larger ones. Slurry preparation for freeze casting is critical. Dispersants are required to distribute ceramic particles homogeneously within the solvent and to ensure slurry stability over time, whereas binders are necessary to prevent the green body from collapsing before sintering.

The final freeze-cast product is the porous scaffold obtained after sublimation of the ice crystals with a three-dimensional, interconnected, and highly aligned porous structure. Handling specimens after sublimation is somewhat difficult, as they have a very low strength. To improve the strength for ceramics and metals, scaffolds are subjected to sintering, which lowers

the porosity level by 10–25% depending on the morphology of the macropores and their local radius of curvature.^[43] The sintering conditions are important for optimizing the physical properties of the scaffold. Once densification is achieved, further increase in the sintering temperature will only increase the grain size. However, the increase of grain size with temperature is very limited, as compared with that observed with materials processed by conventional sintering techniques (e.g., Benaqqa et al.^[44]). This was already observed for freeze-dried ceramics.^[45] Although the underlying reasons for this behavior are not clear, it is probably partly related to the pinning of the grain boundary at the surface during sintering of thin films, when the grain size lies in the same range of order as the lamellae thickness.^[29]

The major limitation of the freeze-casting technique is that it is confined to making rather small (about a centimeter) specimens. Bai et al.^[46] modified the freeze-casting technique by introducing a new bidirectional freezing technique that allows further control of the ice-crystal nucleation and growth as compared with the conventional freeze-casting technique. As a result, a large-scale (several centimeters) nacre-like lamellar structure was successfully produced.

After sintering, interconnected and highly aligned porous layered scaffolds are typically infiltrated with a second phase, resulting in an inorganic–organic layered composite, as shown in Figure 1B. Various nanomaterials, such as polymer chains, nanofibers, or nanosheets, can be directionally frozen and assembled into a lamellar scaffold, as shown in Figure 1C,D. The nanofibers are assembled into a laminar structure by freeze casting, and after sublimation of water, the second phase is infiltrated to form typical layered composites.^[28,47] Recently, nanosheets (including graphene oxide) were also successfully assembled into a layered laminar structure.^[48–50]

Metals do not wet ceramics, so making such materials is complex, particularly for infiltration of a small fraction of metal into a porous ceramic scaffold. Most of the literature describes infiltration with polymers, used as mortars, similar to nacre. The mortar strength (or adhesion of the mortar to the brick) must be such that it is only fractionally smaller than the strength of the bricks themselves; otherwise, the bricks will simply break. Neuendorf et al.^[51] studied the wetting and work of adhesion of seven polymers on hydroxyapatite substrates and found that all of them wet the ceramics, the key requirement for the infiltration. Other requirements for the polymers are low viscosity and a low melting point, while molecular weight does not seem to be an issue. The most commonly used polymer to make nacre-like composites is poly(methyl methacrylate) (PMMA). The details of employing different building blocks for constructing various bioinspired composites are discussed in the following sections.

2.1. Nanoparticles for Assembling Nacre-Inspired Materials by Freeze Casting

The freeze-casting process was originally inspired by the formation of sea ice, during which various impurities and microorganisms migrate into channels between the growing ice crystals. Mimicking the mechanism of sea-ice formation was successfully applied to ceramic nanoparticles for building nacre-like architectures. Deville et al.^[22] were able to create a layered, homogeneous ceramic scaffold whose architecture was a negative replica of the ice, as shown in **Figure 2A**. The thickness of the ceramic layers could be controlled from 1 to 200 μm through the manipulation of the composition of the suspension and the speed of the ice front, as shown in

Figure 2B. The roughness of the ceramic layers (which replicates the roughness of the ice crystals) could be manipulated from the sub-micrometer to the micrometer levels by using various additives. Some particles were trapped in the ice during the freezing process, and generated inorganic bridges between lamellae, whose size and distribution could also be manipulated using additives. The thickness of the lamellar walls linearly decreased as the ice-front velocity increased, and the corresponding cross-sections are shown in **Figure 2B₁–B₄**. After the ice was sublimated, a porous ceramic remained, which was further sintered at a high temperature ($>1000\text{ }^\circ\text{C}$), and a lamellar scaffold structure was obtained with the characteristic roughness generated by the ice dendrites. Then, the pores between the ceramic layers can be filled with other materials to form composites.

Deville et al.^[22] infiltrated epoxy resin into such a freeze-cast hydroxyapatite (HAP) scaffold, as shown in **Figure 2C**. To characterize resistance to failure, fracture-toughness tests were performed on the hybrid ceramics in three-point bending, which showed extensive crack deflection at the interfaces between the ceramic/polymer layers, resulting in very high toughness. This phenomenon also occurs in natural nacre, where it plays an important role in enhancing the toughness at the organic/inorganic interface and preventing cracks across the lamellar structure.

Natural materials usually manipulate adhesion, not only by mechanical, but also by chemical approaches. The roughness of the mineral plates (bricks) and highly specific properties of the organic phase (mortar) in nacre work together, resulting in a damage-tolerant material having exceptional toughness. The multiscale toughening mechanisms in nacre involve viscoplastic energy dissipation within these “mortar” layers and resulting in “pull-out” of mineral bricks.

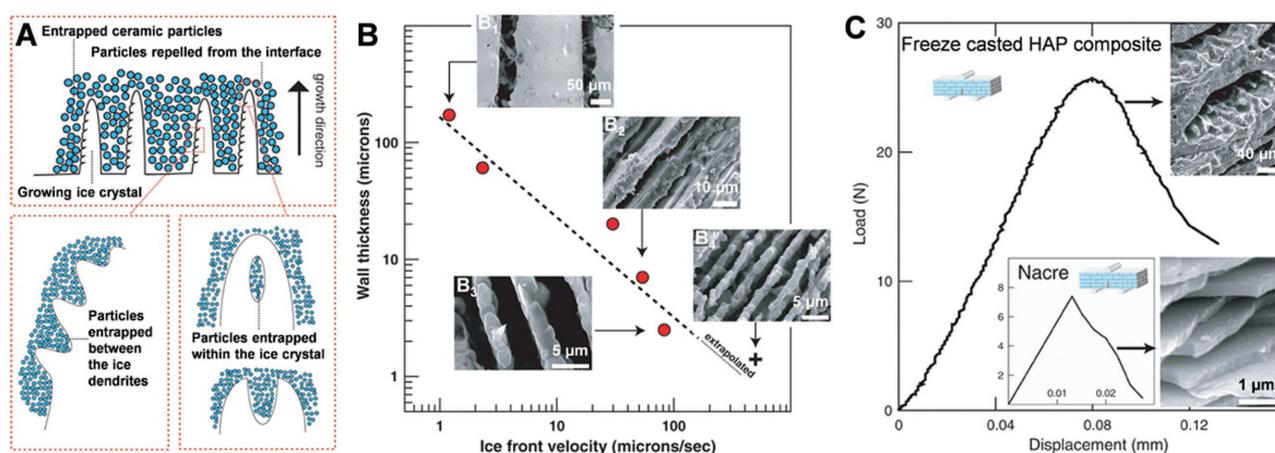


Figure 2. The freeze-casting approach for the fabrication of nacre-like nanocomposites. A) The nanoparticles in the ceramic slurry are expelled by the growing ice crystals during freezing, resulting in a lamellar microstructure in a direction parallel to the freezing front. Tip-splitting leads to a small fraction of the nanoparticles being trapped within the ice crystal. After further sublimation, inorganic bridges between adjacent walls are formed. This porous lamellar ceramic can be infiltrated by a second phase to achieve dense nacre-like nanocomposites. B) An example of an alumina lamellae structure with different wall thicknesses can be achieved by adjusting the freezing speed of the solidification front. The SEM images (B₁) to (B₄) represent cross sections parallel to the direction of movement of the ice front. When the ice front velocity increases, the obtained thickness of lamellar decreases. C) A comparison of mechanical properties of natural nacre and synthetic freeze-cast nacre-like nanocomposites. The freeze-cast HAP–epoxy nacre-like nanocomposites show a very similar load-displacement curve to natural nacre. SEM results (insets) reveal similar features on the fractured surface, with mode-I cracks moving away from the notch and defecting at the lamellae. Reproduced with permission.^[22] Copyright 2006, American Association for the Advancement of Science.

The freeze-casting process is also effective in controlling the morphology of the inorganic layers and the chemistry of the interfaces. Munch et al.^[23] fabricated nacre-like Al₂O₃–PMMA nanocomposites by the freeze-casting technique, as shown in Figure 3A. To achieve enhanced toughness from pull-out mechanisms, in addition to these lamellar structures, more nacre-like brick and mortar structures with a higher ceramic content were made by incorporating a cold-pressing step prior to final sintering and infiltration, as shown in Figure 3B. The bridges obtained during pressing effectively limited sliding of the bricks and provided an additional toughening mechanism in the resultant nanocomposites.

Interfacial interactions could also be enhanced during the freeze-casting process. A methacrylate group was chemically grafted onto the ceramic surfaces before PMMA infiltration using in situ free-radical polymerization during fabrication of Al₂O₃–PMMA lamellar nanocomposites.^[23] The methacrylate groups formed stronger covalent bonding between the Al₂O₃

and PMMA phases. SEM images of the fracture morphology show that the weak boundaries resulted in extensive interface delamination in the Al₂O₃–PMMA lamellae with non-grafted interfaces, as shown in Figure 3D, but the strong boundaries led to much flatter fracture surfaces, as shown in Figure 3E. The grafted interfaces play a key role in enhancing the toughness of brick and mortar nanocomposites, and the in situ imaging of crack propagation clearly shows the pull-out and frictional sliding between ceramic bricks, as shown in Figure 3F. The combination of grafted interfaces and bridges in the brick-and-mortar nanocomposites greatly improved the bending strength, as shown in Figure 3G. The nacre-like Al₂O₃–PMMA materials also displayed remarkable R-curve behavior, indicating their tolerance to the stable growth of cracks, with a fracture toughness of 30 MPa m^{0.5} or more (as shown in Figure 3H), some 300 times higher (in energy terms) than either the ceramic (alumina) or polymer (PMMA), and an order of magnitude higher than that which can be expected from the “rule of mixtures.”

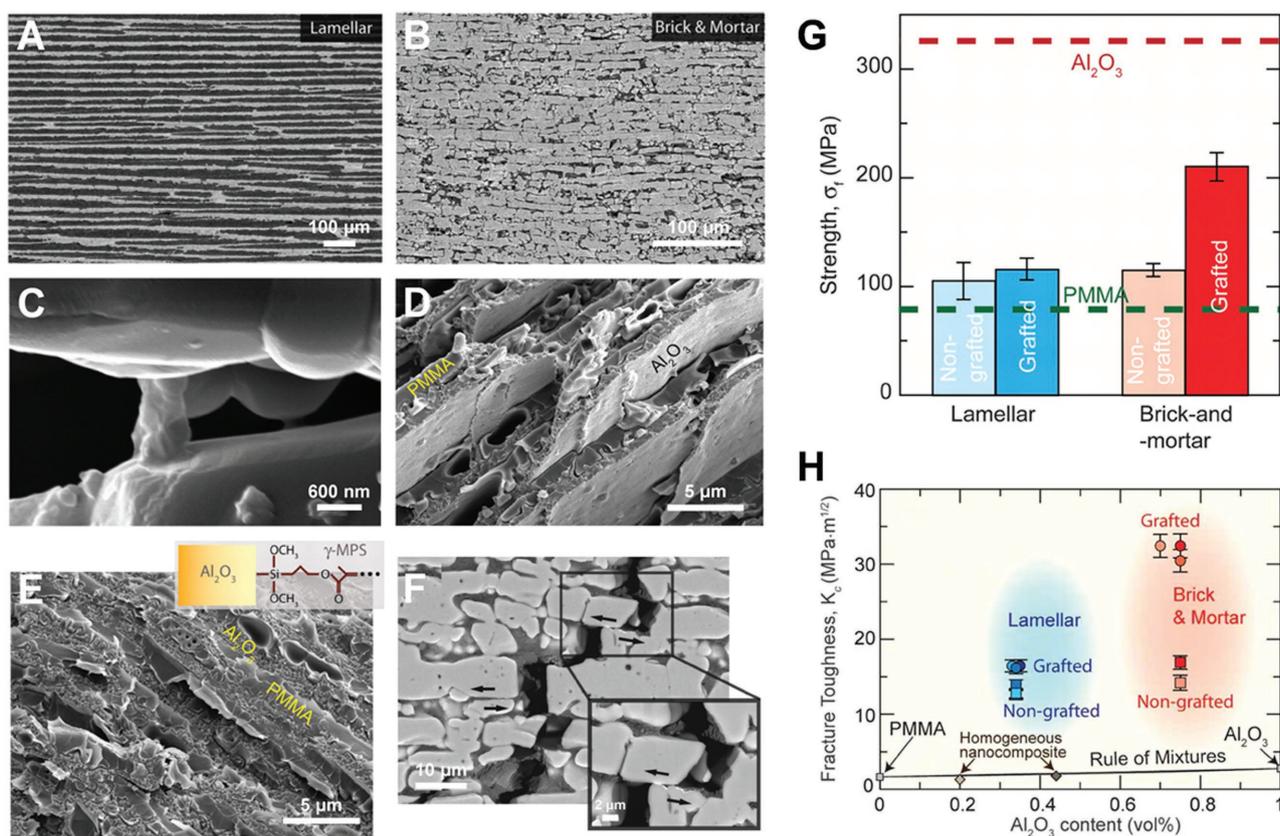


Figure 3. A) The nacre-like Al₂O₃/PMMA lamellar nanocomposites fabricated by freeze casting employing nanoparticles and followed by polymer infiltration (the light phase is the Al₂O₃, and the dark phase is the PMMA). B) The Al₂O₃/PMMA lamellar nanocomposites were further pressed and sintered to achieve brick-and-mortar architectures with high ceramic contents (up to 80 vol%). C) The ceramic bridges between lamellae are formed of the trapped ceramic nanoparticles by growing ice between the lamellae or bricks during the second sintering steps. These bridges limit sliding of the lamellae, providing effective toughening. D) The Al₂O₃/PMMA lamellar nanocomposites without grafted interfaces show extensive interface delamination during fracture. E) Strong interfaces are formed after chemical grafting, resulting in much flatter fracture surfaces. F) Pull-out and frictional sliding between the ceramic bricks are observed in in situ imaging of the crack propagation in brick-and-mortar nanocomposites. The arrows indicate the direction of sliding. G) A bending strength comparison of lamellar and brick and mortar nanocomposites shows that the chemical grafting interface dramatically enhances the strength compared with the non-grafted interface. H) The fracture toughness can also be greatly improved by chemical grafting interfaces in the lamellar and the brick-and-mortar nanocomposites, compared with their constituent materials. For example, the fracture toughness of nanocomposites with a brick-and-mortar structure is more than an order of magnitude larger than their principle constituent phase of Al₂O₃. Reproduced with permission.^[23] Copyright 2008, American Association for the Advancement of Science.

The fracture resistance of many natural materials increases with crack extension, generating a characteristic rising crack resistance curve (*R*-curve). In other words, these materials do not fail catastrophically. Since replicating natural materials' fracture resistance is one of the goals in developing nacre-like synthetic materials, numerous papers describing such synthetic materials^[18,23,52] report not only a conventional measure of the toughness, such as the crack-initiation toughness K_{IC} , but also the *R*-curve toughness. The *R*-curve data show that the toughness in these materials is developed during crack growth and not during crack initiation. The *R*-curve behavior is characteristic of many bioinspired ceramic structures, giving us a better understanding of how they can sustain subcritical cracking, thus delaying or even inhibiting catastrophic failure.

The key question is whether the properties of these nanocomposites can be further improved. Modeling by Begley and co-workers^[53,54] suggests that further improvements are possible. In theory, with a mortar yield strength of 50 MPa, ceramic bricks measuring $\approx 20 \times 1 \mu\text{m}$ with a strength of ≈ 1 GPa, and interfacial sliding displacements of ≈ 75 nm, a two-fold increase in strength and toughness should be achievable.^[54] In short, a reduction in soft mortar content and the use of finer-scale bricks made from a stronger ceramic (for example, SiC and Si₃N₄) is needed for further improvement of strength and to provide additional toughening mechanisms. Unfortunately, SiC and Si₃N₄ present great experimental difficulties due to the extremely high processing temperatures required.

2.2. Nanofibers for Assembling Bioinspired Materials by Freeze Casting

Ferraro et al.^[55] reported that SiC fibers can be assembled into highly porous networks by the freeze-casting technique, as shown in Figure 4A. After sintering at 1800 °C under an argon atmosphere, the resultant scaffold showed a structure with a highly interconnected porosity and a hierarchical architecture with aligned thin and porous ceramic layers. The network struts and architecture formed by the SiC fibers could be manipulated by adjusting the composition of the suspension and the freezing conditions. The interlayer distance of this unique hierarchical architecture varied between 15 and 50 μm . As the freezing rate increased, the interlayer distances decreased, as shown in Figure 4B. The suspension with 1.5 vol% fibers could be assembled into a layered network after sintering into a structure with 98% porosity, as shown in Figure 4C. The walls were assembled by entangled fibers and had a thickness of only ≈ 1 –2 μm , as shown in Figure 4D. Like hard SiC fibers, other natural soft nanofibers can also be assembled into a lamellar structure by the freeze-casting technique. Si et al.^[56] used a novel biomass—konjac glucomannan (KGM)—and flexible SiO₂ nanofibers to create carbonaceous nanofibrous aerogels (CNFAs) with an ordered honeycomb-like structure. The fabrication process is illustrated in Figure 4E. The KGM/SiO₂ nanofiber composite aerogels were first assembled by the freeze-casting technique, and, after carbonization, CNFAs with hierarchical structure were achieved, as shown in Figure 4F. Experimental results have shown that CNFAs exhibit intriguing properties, such as low density, super cyclic compressibility, good thermal stability, and elastic-responsive conductivity.

An example of extremely high-porosity scaffolds obtained by freeze casting of V₂O₅ nanofibers, closely resembling that of cuttlebone, has been recently reported.^[57] By adjusting the initial V₂O₅ nanofiber concentration, the mechanical performance of scaffolds can be easily tuned. The V₂O₅ scaffolds features regularly distributed, porous pillars, which connect adjacent nanometer-ranged thick lamellae, forming rectangular, micrometer-sized cavities, resulting in ultrahigh porosity of 99.8%. Such an approach can be easily applied to other ceramic fibers for the fabrication of ultralight structures with unique mechanical and functional properties in practical dimensions. The combination of large surface area with good mechanical properties makes such structures useful for energy-storage devices, tissue-engineering applications, sensors, and catalysts.

2.3. Freeze Casting of Macromolecules to Fabricate Porous Structures

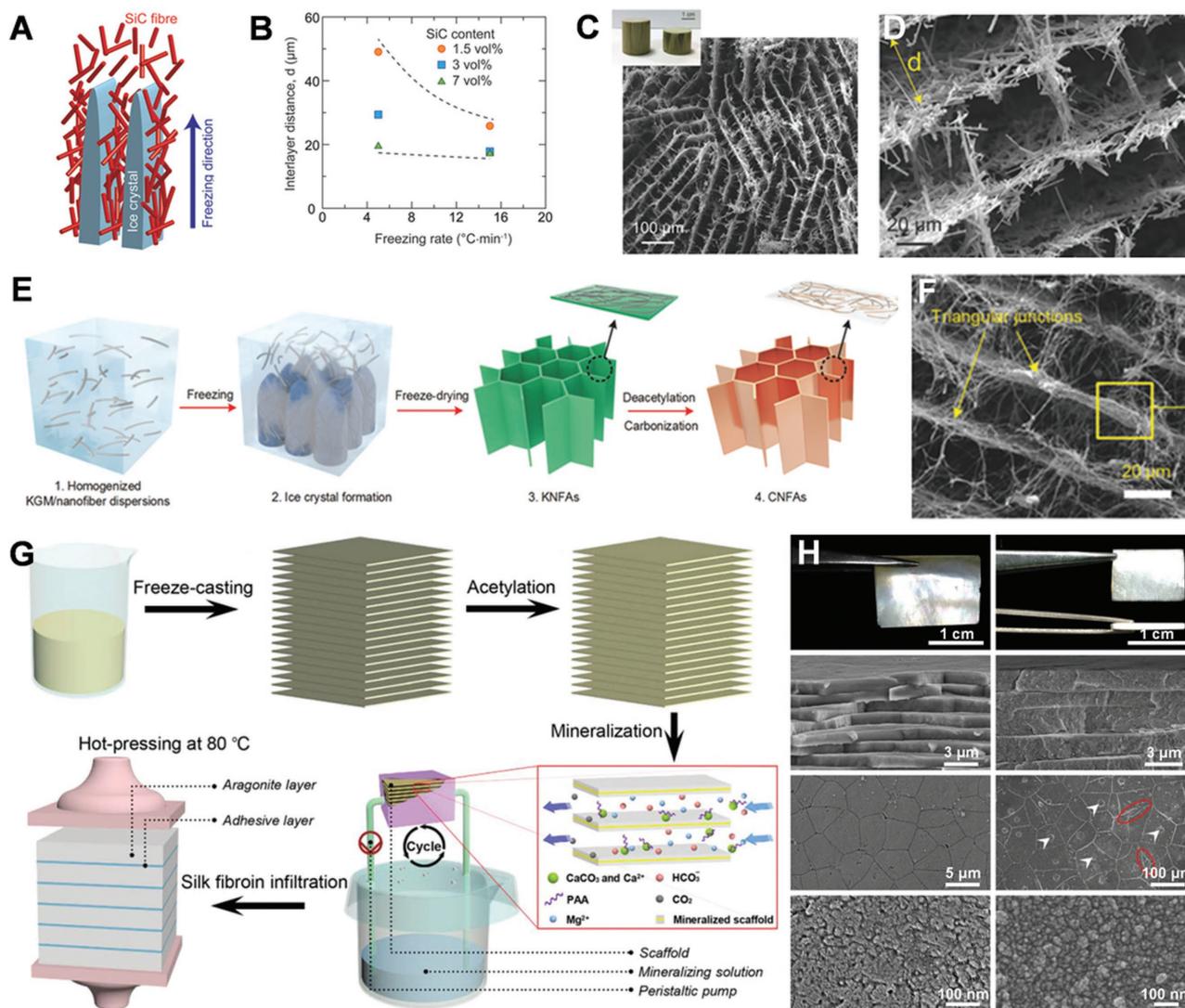
Scaffolds composed of the nano-/microfibers described previously also demonstrate the freeze-casting technique's possibility for constructing lamellar scaffolds with polymer chains or macromolecules. Directional freezing of silk scaffolds for tissue engineering,^[58] cellulose nanofibers,^[59] soy protein,^[60] and several other macromolecules have been reported in the literature. However, nacre-like nanocomposites based on a scaffold assembled with polymer chains by the freeze-casting technique have so far not been accomplished.

Zhang et al.^[47] demonstrated that water-soluble polymer macromolecules, such as poly(vinyl alcohol) and polycaprolactone, can be assembled into a lamellar scaffold using the freeze-casting technique. They employed the directional-freezing technique to produce aligned porous materials that could be useful for tissue-engineering applications.

Recently, Mao et al.^[61] applied the freeze-casting technique to assemble chitosan into a lamellar structure, which was subsequently acetylated and transformed to β -chitin. The laminated structure was next mineralized via the decomposition of Ca(HCO₃)₂ in the presence of poly(acrylic acid) and Mg²⁺. After hot pressing, synthetic nacre was obtained, as shown in Figure 4G. The weight percent of CaCO₃ in the laminated composite reached up to 91 wt%. The resultant synthetic nacre shows similarities in structure to natural nacre from macro- to nanoscale dimensions, as shown in Figure 4H. Compared with previous nacre-like nanocomposites made through freezing ceramic nanoparticles,^[23] this "assembly-and-mineralization" mesoscale approach provides an alternative way to fabricate lamellar nacre-like materials. The main issues with the technique are that it is slow and produces only millimeter-sized specimens with mechanical properties (strength and toughness) that fall short of natural nacre's. However, this research clearly shows that mineralization could be, in principle, an effective process for making novel materials.

2.4. Nanosheets for Assembling Nacre-Inspired Materials by Freeze Casting

Besides nanoparticles and macromolecules, the freeze-casting technique is also suitable for assembling nanosheets into a



scaffold for constructing nacre-like materials. For example, Qiu et al.^[50] first applied the freeze-casting technique to assemble partially reduced graphene oxide (pr-GO) into a lamellar hierarchical structure, as shown in Figure 5A. After further reduction, the obtained biomimetic pr-GO-based structure exhibited integrated properties of ultralow density, superelasticity, and good electrical conductivity. This nacre-like rGO scaffold can be further infiltrated with a second phase to fabricate nacre-like nanocomposites. For example, D'Elia et al.^[48] first infiltrated a solution of poly(dimethylsiloxane) (PDMS) and boron oxide (B_2O_3) nanoparticles into the rGO scaffold, as shown in Figure 5B. During heating, the PDMS/ B_2O_3 crosslinked into

the polymer of poly(borosiloxane) (PBS), which is a supramolecular polymer with an intrinsic self-healing character. Then, nacre-like, self-healing, graphene-based nanocomposites were achieved.

Recently, Picot et al.^[49] infiltrated poly(methylsiloxane), a pre-ceramic polymer, into a graphene-based scaffold assembled by the freeze-casting technique. After heating up to 1000 °C, the siloxane polymers were converted into a silicon oxycarbide glass, resulting in the shrinkage of the graphene-based scaffolds. The structure morphology of the resultant nacre-like graphene-based ceramic nanocomposite is shown in Figure 5C (parallel to the ice-growth direction) and Figure 5D (perpendicular). The

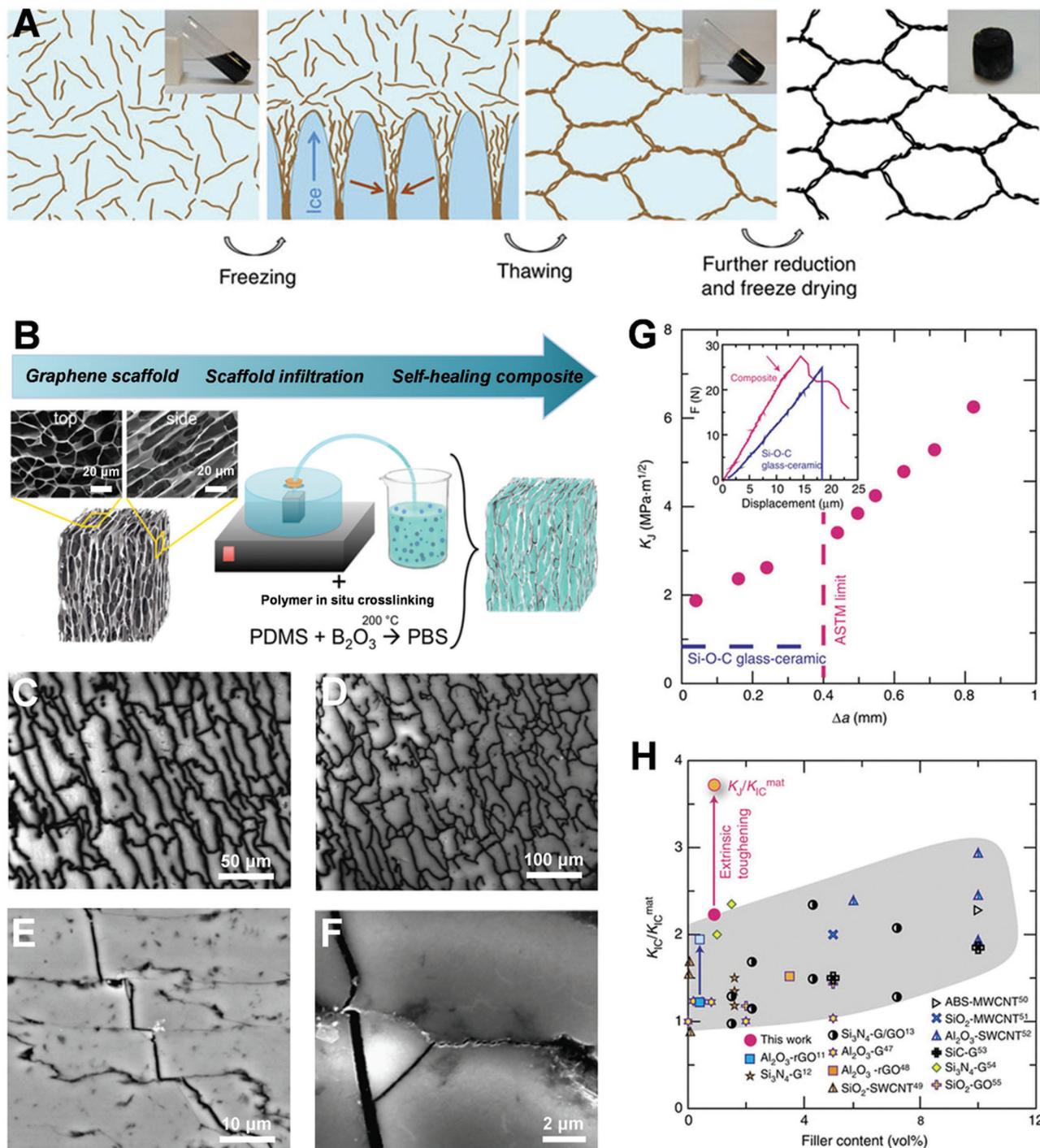


Figure 5. Nacre-like nanocomposites assembled by graphene nanosheets through the freeze-casting technique. A) A schematic illustration of a lamellar graphene scaffold created by the freeze-casting technique. A dispersion of rGO nanosheets was frozen first, then the rGO nanosheets were expelled along the growth direction of ice crystal. After sublimation of the ice crystals and further reduction, the graphene lamellar networks were obtained. Then the nacre-like graphene-lamellae-based nanocomposites could be achieved after infiltrating a second phase, such as a soft or hard phase. B) The rGO lamellar networks were infiltrated by a soft PDMS/B₂O₃ solution. After crosslinking of PBS by heating, nacre-like self-healing nanocomposites were obtained. The ceramic precursor mixture was infiltrated into the rGO network. C, D) After sintering at a high temperature, the laminated rGO–Si–O–C nanocomposites were obtained: parallel to the ice growth direction (C) and perpendicular to it (D). E, F) The rGO–Si–O–C shows outstanding mechanical properties due to the lamellar networks of rGO nanosheets, and several toughening mechanisms could be identified through SEM images, including crack deflection (E) and interfacial friction (F). G) This unique structure results in stable crack-propagation with a rising resistance curve. H) Compared with other ceramics reinforced with carbon nanostructures, this interconnected network offers very efficient toughening at extremely low carbon contents. A) Reproduced with permission.^[50] Copyright 2012, Nature Publishing Group. B) Reproduced with permission.^[48] Copyright 2016, Wiley-VCH. C–G) Reproduced with permission.^[49] Copyright 2017, Nature Publishing Group.

laminated architecture promotes microcracking, and the typical crack deflection is easily identified in the propagating crack shown in Figure 5E. Other crack branching and interfacial friction, shown in Figure 5F, are also observed in the crack propagation. This combination of several toughening mechanisms would result in extraordinary toughness. Compared with glass–ceramic, the initiation toughness of ceramic–rGO nanocomposites is two times higher. Stable crack propagation was achieved with 1 vol% of carbon in ceramic–rGO nanocomposites, which also exhibit a rising *R*-curve behavior with a steady rise of K_I , as shown in Figure 5G. The resulting maximum toughness is almost 3.8 times higher than that of pure glass–ceramic, but 14 times higher in terms of energy. Compared with the fracture resistance of other ceramics reinforced with carbon nanostructures, ceramic–rGO nanocomposites exhibit efficient toughening with extremely low carbon contents, and show several times better toughness, as shown in Figure 5H.

Other nanosheets can also be assembled into the scaffold for constructing nacre-bioinspired structural materials. For example, Hunger et al.^[62] used directional solidification during freeze casting of platelet-based slurries for the development of highly porous honeycomb-like scaffolds with a nacre-like cell-wall structure, which arises from the self-assembly of the ceramic (alumina) platelets during processing. Such “porous nacre” possesses properties considerably higher than those of composite scaffolds of the same composition and overall porosity made with spherical particles. Bouville et al.^[52] demonstrated strong, tough, and stiff nacre-bioinspired ceramics based on alumina platelets and a glass precursor. They applied the freeze-casting technique to assemble the alumina platelets into a lamellar scaffold and incorporated glass precursors instead of a ductile phase. The alumina nanoparticles served as a source of both inorganic bridges and nanoasperities at the surface of the platelets, similar to nacre. Then, glass precursors (silica and calcia) were also infiltrated into the remaining gaps during the sintering process. With sintering at a high temperature, the alumina nanoparticles formed strong bridges between adjacent platelets. The unique architecture and the interfacial structure of these nacre-like alumina materials resulted in a combination of mechanisms, including crack deflection, crack bridging, crack branching, and delamination.

3. Conclusions and Outlook

The last few decades have seen astounding growth in the sheer number of research papers dealing with the microstructure and properties of natural materials. Bone and nacre have been especially recognized for their excellent mechanical properties, but mimicking them and other natural structures is a task of enormous technical complexity for which clear guidelines do not exist. Successful bioinspired bulk structural materials with new or improved properties remain rare. The vast majority of current processing techniques yield materials with functional properties that are disappointing when compared with those of natural biomaterials. The benefits of trying, though, are immense. Numerous processing techniques have been proposed to produce nacre-like and bone-like materials. However, frequently the processes employed have been limited to making

a few thick ($\approx 200 \mu\text{m}$) ceramic layers that are not yet suitable for structural applications. Still, we believe that freeze casting, combined with hot-press-assisted methods, has great potential. These are probably the techniques best suited to producing large-sized materials in bulk.

Freeze casting has been demonstrated to be suitable for assembling all kinds of nanomaterials, such as nanoparticles, polymer chains or nanofibers, and nanosheets, into lamellar scaffolds. It is a highly effective approach for controlling the micro-/nanoscale hierarchical layered structure, including bridges between the lamellar layers, and interfacial interactions. Recently, the bidirectional freezing technique has been explored for successfully achieving a large-scale lamellar ceramic structure,^[46] indicating that the approach is an effective way of manufacturing bulk bioinspired structural materials.

Nevertheless, mimicking nacre still remains a “grand challenge”, as assembling a precise structure and emulating its unique interfacial interactions is difficult. Finding ways to make structural materials in nature’s image in the bulk form, in which they can be used in practice, is still far from a true engineering reality. The remaining challenge is to precisely control the scaffold architecture and obtain the highest possible volume fraction, close to natural nacre, while designing synergistic interfacial interactions to achieve integrated high strength and toughness. To achieve that, freeze casting should be combined with other approaches, like 3D printing or mineralization, to precisely manipulate the architecture, structure, and interfacial interactions of nacre-like materials.

The freeze-casting technique is also being investigated for the development of novel batteries and supercapacitors.^[63–65] These devices require lamellar structures with scalable high-density, low-tortuosity, porous electrode designs. Successful design using graphene-based materials, for example, would enable increased cell-level energy density compared with conventional Li-ion technology. Using freeze casting combined with filtration, Shao et al.^[63] synthesized 3D porous graphene films, creating a high-performance supercapacitor with a highly porous microstructure, superior electrical conductivity, and exceptional mechanical strength. The device exhibited both very high power densities and very high energy densities. Significant research efforts in this area have only begun.

From the perspective of new energy-related materials, the true pay-off would be in developing high-temperature, lightweight materials that do not suffer from the ubiquitous brittle characteristics of ceramics. The major issue with natural materials is that they do not have high temperature resistance or capability. The nanocomposites described here all contain a polymeric or organic matrix, and therefore can be used only for low-temperature applications. As an incredible number of excellent synthetic materials for low-temperature applications already exist, the bioinspired or nacre-like approach may not be that useful in making new ones.

For many devices (such as turbines, airplane engines, and power generators) that operate at high temperatures, efficiency is directly linked to how hot they can operate. Higher-temperature operation results not only in greater efficiencies, but also in less fuel consumption and reduced environmental pollution. For these applications, we need new, lightweight, and damage-tolerant materials. This can only be accomplished

using ceramic–matrix composites (CMCs). General Electric, for example, has developed a SiC CMC for turbine blades that is one third the weight of nickel superalloys, yet extremely durable.^[66] However, it took 30 years to perfect the manufacturing of this CMC. Here is an area where the bioinspired approach could lead to breakthroughs in making new materials. Such materials could be simpler in architecture and cheaper to manufacture. The idea here is to seek higher ceramic volume fractions with finer bricks within a nacre-like brick-and-mortar architecture, which we predict would result in toughness properties approaching that of the Al₂O₃ and SiC hybrids, but with higher strength. A true breakthrough would be to make high-volume-fraction ceramics containing small amounts of a metallic phase within a carefully controlled structural architecture, but this represents quite a challenge, in part because of the high wetting angles for metals on ceramics. Such materials would be extremely useful for high-temperature applications.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Nat. Mater.* **2015**, *14*, 23.
- [2] M. A. Meyers, P. Y. Chen, A. Y. M. Lin, Y. Seki, *Prog. Mater. Sci.* **2008**, *53*, 1.
- [3] F. Barthelat, Z. Yin, M. J. Buehler, *Nat. Rev. Mater.* **2016**, *1*, 1.
- [4] Q. F. Cheng, L. Jiang, Z. Y. Tang, *Acc. Chem. Res.* **2014**, *47*, 1256.
- [5] S. S. Gong, H. Ni, L. Jiang, Q. Cheng, *Mater. Today* **2017**, *20*, 210.
- [6] P. Podsiadlo, A. K. Kaushik, E. M. Arruda, A. M. Waas, B. S. Shim, J. D. Xu, H. Nandivada, B. G. Pumphlin, J. Lahann, A. Ramamoorthy, N. A. Kotov, *Science* **2007**, *318*, 80.
- [7] Z. Tang, N. A. Kotov, S. Magonov, B. Ozturk, *Nat. Mater.* **2003**, *2*, 413.
- [8] Q. F. Cheng, M. X. Wu, M. Z. Li, L. Jiang, Z. Y. Tang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3750.
- [9] H. B. Yao, H. Y. Fang, Z. H. Tan, L. H. Wu, S. H. Yu, *Angew. Chem. Int. Ed.* **2010**, *49*, 2140.
- [10] H. B. Yao, Z. H. Tan, H. Y. Fang, S. H. Yu, *Angew. Chem. Int. Ed.* **2010**, *49*, 10127.
- [11] W. Cui, M. Li, J. Liu, B. Wang, C. Zhang, L. Jiang, Q. Cheng, *ACS Nano* **2014**, *8*, 9511.
- [12] A. Chavez-Valdez, M. S. P. Shaffer, A. R. Boccaccini, *J. Phys. Chem. B* **2013**, *117*, 1502.
- [13] Z. Xiong, C. Liao, W. Han, X. Wang, *Adv. Mater.* **2015**, *27*, 4469.
- [14] M. Zhang, L. Huang, J. Chen, C. Li, G. Shi, *Adv. Mater.* **2014**, *26*, 7588.
- [15] M. Zhang, Y. Wang, L. Huang, Z. Xu, C. Li, G. Shi, *Adv. Mater.* **2015**, *27*, 6708.
- [16] A. Walther, I. Bjurhager, J. M. Malho, J. Pere, J. Ruokolainen, L. A. Berglund, O. Ikkala, *Nano Lett.* **2010**, *10*, 2742.
- [17] A. Walther, I. Bjurhager, J. M. Malho, J. Ruokolainen, L. Berglund, O. Ikkala, *Angew. Chem. Int. Ed.* **2010**, *49*, 6448.
- [18] H. Le Ferrand, F. Bouville, T. P. Niebel, A. R. Studart, *Nat. Mater.* **2015**, *14*, 1172.
- [19] I. Corni, T. J. Harvey, J. A. Wharton, K. R. Stokes, F. C. Walsh, R. J. K. Wood, *Bioinspiration Biomimetics* **2012**, *7*, 1.
- [20] W. B. Hardy, *Proc. R. Soc. Lond., Ser. A* **1926**, *112*, 47.
- [21] T. Moran, *Proc. R. Soc. Lond., Ser. A* **1926**, *112*, 30.
- [22] S. Deville, E. Saiz, R. K. Nalla, A. P. Tomsia, *Science* **2006**, *311*, 515.
- [23] E. Munch, M. E. Launey, D. H. Alsem, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Science* **2008**, *322*, 1516.
- [24] S. Deville, *Adv. Eng. Mater.* **2008**, *10*, 155.
- [25] S. Deville, *Materials* **2010**, *3*, 1913.
- [26] Q. Fu, E. Saiz, M. N. Rahaman, A. P. Tomsia, *Adv. Funct. Mater.* **2013**, *23*, 5461.
- [27] U. G. K. Wegst, M. Schecter, A. E. Donius, P. M. Hunger, *Philos. Trans. R. Soc. A* **2010**, *368*, 2099.
- [28] S. Deville, *J. Mater. Res.* **2013**, *28*, 2202.
- [29] S. Deville, E. Saiz, A. P. Tomsia, *Biomaterials* **2006**, *27*, 5480.
- [30] S. Deville, E. Saiz, A. P. Tomsia, *Acta Mater.* **2007**, *55*, 1965.
- [31] Q. Fu, M. N. Rahaman, F. Dogan, B. S. Bal, *Biomed. Mater.* **2008**, *3*.
- [32] Q. Fu, M. N. Rahaman, F. Dogan, B. S. Bal, *J. Biomed. Mater. Res. B* **2008**, *86B*, 514.
- [33] Q. Fu, M. N. Rahaman, F. Dogan, B. S. Bal, *J. Biomed. Mater. Res. B* **2008**, *86B*, 125.
- [34] Y. H. Koh, I. K. Jun, J. J. Sun, H. E. Kim, *J. Am. Ceram. Soc.* **2006**, *89*, 763.
- [35] Y. H. Koh, E. J. Lee, B. H. Yoon, J. H. Song, H. E. Kim, H. W. Kim, *J. Am. Ceram. Soc.* **2006**, *89*, 3646.
- [36] A. Macchetta, I. G. Turner, C. R. Bowen, *Acta. Biomater.* **2009**, *5*, 1319.
- [37] J. W. Moon, H. J. Hwang, M. Awano, K. Maeda, *Mater. Lett.* **2003**, *57*, 1428.
- [38] E. Munch, E. Saiz, A. P. Tomsia, S. Deville, *J. Am. Ceram. Soc.* **2009**, *92*, 1534.
- [39] T. Waschkies, R. Oberacker, M. J. Hoffmann, *J. Am. Ceram. Soc.* **2009**, *92*, S79.
- [40] N. O. Shanti, K. Araki, J. W. Halloran, *J. Am. Ceram. Soc.* **2006**, *89*, 2444.
- [41] S. Deville, E. Maire, G. Bernard-Granger, A. Lasalle, A. Bogner, C. Gauthier, J. Leloup, C. Guizard, *Nat. Mater.* **2009**, *8*, 966.
- [42] C. Korber, G. Rau, M. D. Cosman, E. G. Cravalho, *J. Cryst. Growth* **1985**, *72*, 649.
- [43] S. Deville, G. Bernard-Granger, *J. Eur. Ceram. Soc.* **2011**, *31*, 983.
- [44] C. Benaqqa, J. Chevalier, M. Saadaoui, G. Fantozzi, *Biomaterials* **2005**, *26*, 6106.
- [45] H. Lu, Z. Qu, Y. C. Zhou, *J. Mater. Sci.: Mater. Med.* **1998**, *9*, 583.
- [46] H. Bai, Y. Chen, B. Delattre, A. P. Tomsia, R. O. Ritchie, *Sci. Adv.* **2015**, *1*, e1500849.

- [47] H. F. Zhang, I. Hussain, M. Brust, M. F. Butler, S. P. Rannard, A. I. Cooper, *Nat. Mater.* **2005**, *4*, 787.
- [48] E. D'Elia, S. Barg, N. Ni, V. G. Rocha, E. Saiz, *Adv. Mater.* **2015**, *27*, 4788.
- [49] O. T. Picot, V. G. Rocha, C. Ferraro, N. Ni, E. D'Elia, S. Meille, J. Chevalier, T. Saunders, T. Peijs, M. J. Reece, E. Saiz, *Nat. Commun.* **2017**, *8*, 14425.
- [50] L. Qiu, J. Z. Liu, S. L. Y. Chang, Y. Wu, D. Li, *Nat. Commun.* **2012**, *3*, 1241.
- [51] R. E. Neuendorf, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Acta. Biomater.* **2008**, *4*, 1288.
- [52] F. Bouville, E. Maire, S. Meille, B. Van de Moortele, A. J. Stevenson, S. Deville, *Nat. Mater.* **2014**, *13*, 508.
- [53] M. R. Begley, N. R. Philips, B. G. Compton, D. V. Wilbrink, R. O. Ritchie, M. Utz, *J. Mech. Phys. Solids.* **2012**, *60*, 1545.
- [54] D. V. Wilbrink, M. Utz, R. O. Ritchie, M. R. Begley, *Appl. Phys. Lett.* **2010**, *97*, 193701.
- [55] C. Ferraro, E. Garcia-Tuñón, V. G. Rocha, S. Barg, M. D. Fariñas, T. E. G. Alvarez-Arenas, G. Sernicola, F. Giuliani, E. Saiz, *Adv. Funct. Mater.* **2016**, *26*, 1636.
- [56] Y. Si, X. Q. Wang, C. C. Yan, L. Yang, J. Y. Yu, B. Ding, *Adv. Mater.* **2016**, *28*, 9512.
- [57] A. Knoller, T. Runcevski, R. E. Dinnebier, J. Bill, Z. Burghard, *Sci. Rep.* **2017**, *7*.
- [58] B. B. Mandal, E. S. Gil, B. Panilaitis, D. L. Kaplan, *Macromol. Biosci.* **2013**, *13*, 48.
- [59] Z. Z. Pan, H. Nishihara, S. Iwamura, T. Sekiguchi, A. Sato, A. Isogai, F. Y. Kang, T. Kyotani, Q. H. Yang, *ACS Nano* **2016**, *10*, 10689.
- [60] J. A. Guan, D. Porter, K. Tian, Z. Z. Shao, X. Chen, *J. Appl. Polym. Sci.* **2010**, *118*, 1658.
- [61] L.-B. Mao, H.-L. Gao, H.-B. Yao, L. Liu, H. Cölfen, G. Liu, S.-M. Chen, S.-K. Li, Y.-X. Yan, Y.-Y. Liu, S.-H. Yu, *Science* **2016**, *354*, 107.
- [62] P. M. Hunger, A. E. Donius, U. G. K. Wegst, *J. Mech. Behav. Biomed.* **2013**, *19*, 87.
- [63] Y. Shao, M. F. El-Kady, C.-W. Lin, G. Zhu, K. L. Marsh, J. Y. Hwang, Q. Zhang, Y. Li, H. Wang, R. B. Kaner, *Adv. Mater.* **2016**, *28*, 6719.
- [64] M.-Q. Zhao, Q. Zhang, J.-Q. Huang, G.-L. Tian, J.-Q. Nie, H.-J. Peng, F. Wei, *Nat. Commun.* **2014**, *5*, 3410.
- [65] S. Behr, R. Amin, Y.-M. Chiang, A. P. Tomsia, *Process Eng. DKG* **2015**, *92*, E39.
- [66] "Stubborn GE Scientist Creates New Fuel-Saving Material, Jonathan Fahey", The Associated Press, <http://www.dailynews.com/science/20150514/Stubborn-GE-Scientist-Creates-New-Fuel-Saving-Material> (accessed: May 2015).