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Bioinspired structural materials

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Natural structural materials are built at ambient temperature from a fairly limited selection of components. They usually comprise hard and soft phases arranged in complex hierarchical architectures, with characteristic dimensions spanning from the nanoscale to the macroscale. The resulting materials are lightweight and often display unique combinations of strength and toughness, but have proven difficult to mimic synthetically. Here, we review the common design motifs of a range of natural structural materials, and discuss the difficulties associated with the design and fabrication of synthetic structures that mimic the structural and mechanical characteristics of their natural counterparts.

The technological development of humanity was supported in its early stages by natural materials such as bone, wood and shells. As history advanced, these materials were slowly replaced by synthetic compounds that offered improved performance. Today, scientists and engineers continue to be fascinated by the distinctive qualities of the elegant and complex architectures of natural structures, which can be lightweight and offer combinations of mechanical properties that often surpass those of their components by orders of magnitude. Contemporary characterization and modelling tools now allow us to begin deciphering the intricate interplay of mechanisms acting at different scales — from the atomic to the macroscopic — and that endow natural structures with their unique properties. At present, there is a pressing need for new lightweight structural materials that are able to support more efficient technologies that serve a variety of strategic fields, such as transportation, buildings, and energy storage and conversion. To address this challenge, yet-to-be-developed materials that would offer unprecedented combinations of stiffness, strength and toughness at low density, would need to be fashioned into bulk complex shapes and manufactured at high volume and low cost. It is an open question how this goal can be achieved. Although remarkable examples have arisen from the laboratory, it remains uncertain whether they can be scaled-up for use in practical applications.

It is a classic materials-design problem that the two key structural properties — strength and toughness — tend to be mutually exclusive (Box 1); strong materials are invariably brittle, whereas tough materials are frequently weak[1]. Here is where natural organisms provide a rich source of inspiration for fresh ideas. They provide an opportunity for us to benefit from the great number and considerable diversity of solutions, perfected over millions of years of evolution[2]. For example, highly mineralized, mostly ceramic, natural structures, such as tooth enamel or nacre, minimize wear and provide protection. A unique aspect of these materials is that they utilize different structures or structural orientations, to generate hard surface layers so as to resist wear and/or penetration, and have a tough subsurface to accommodate the increased deformation; that is, unlike human-made hard materials such as ceramics, they are designed for total fracture resistance. Specifically, they arrest crack propagation and avoid catastrophic failure. Other examples of evolution-driven strategies are the use of highly porous architectures in materials that must combine light weight and stiffness, such as cancellous bone or bamboo. However, stiff and porous structures tend to be weak. To maintain strength, some natural materials feature complex designs that frequently incorporate nanofibres and intricate architectural gradients. In contrast to most human-engineered materials, such natural materials are built at ambient temperatures through bottom-up strategies that are difficult to duplicate in large-scale manufacturing[2]. Most importantly, natural materials that combine the desirable properties of their components often perform significantly better than the sum of their parts — an advantage that has sparked much of the current interest in bioinspired materials design. In particular, they offer a path towards solving the challenge of designing materials that are both strong and tough, through the development of a confluence of mechanisms that interact at multiple length scales, from the molecular to the macroscopic. Hybrid materials that are highly mineralized (such as seashells, bone and teeth), lightly mineralized (such as fish scales and lobster cuticle) and purely polymeric (such as insect cuticle, wood, bamboo or silk) are prime examples of natural composites with properties that far exceed those of their material constituents.

Mimicking the features of a natural material is not a trivial undertaking. Many investigators have characterized the nano/microstructure of a wide variety of natural structural materials — ranging from wood, antler, bone and teeth, to silk, fish scales, bird beaks and shells. Yet few have comprehensively characterized the most critical mechanical properties of these materials, such as strength and toughness. Fewer still have identified the salient nano/microscale mechanisms underlying such properties. Equally important, there are even fewer examples so far of practical synthetic versions of these materials. Consequently, critics have suggested that the field has been largely unsuccessful in its quest to apply bioinspired strategies to engineering materials and design[3]. However, as exemplified by the development of nacre-inspired materials, the first steps have been taken in characterization, modelling and manufacturing. Such progress is fuelling the growing conviction that highly damage-tolerant bioinspired structures can be designed and built.

Because natural materials typically feature a limited number of components that have relatively poor intrinsic properties, superior traits stem from naturally complex architectures that encompass multiple length scales. In contrast, most engineered materials have been developed through the formulation and synthesis of new compounds, and with structural control primarily at the micrometre scale. Consequently, it has been claimed that nanotechnology is opening a spectrum of possibilities by allowing the manipulation of materials at previously unattainable dimensions. However,

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with respect to complex mechanical properties such as fracture toughness — for which characteristic length scales are orders of magnitude larger — an exclusive focus on the nanoscale would be far too limited. Any rational strategy must incorporate nano-, micro- and macroscale features, and thus involve the so-called mesoscale approach.

To accomplish this, one must extract the key design parameters from natural structures — that is, their natural design motifs

Box 1 | Essentials of mechanical properties.

The mechanical properties of materials describe their ability to withstand applied loads and displacements. The fundamental relationship underlying these properties is the constitutive law, which relates the strain (normalized relative displacement) that a material experiences to an applied stress (load normalized by area). This relationship can be defined to embrace many modes of deformation behaviour, such as elasticity (reversible), plasticity (permanent) or rate-dependent deformation (for example, viscoelasticity or high-temperature creep), and in principle can be established at any length scale. However, it is generally measured using a uniaxial tensile test, whereby a sample is loaded in tension (or compression), and the (normal) strains are measured as a function of the applied (normal) stress to determine properties such as stiffness, strength, ductility and toughness.

Stiffness is related to the elastic modulus, and defines the force required to produce elastic deformation; as such, Young's modulus E is defined by the initial slope of the uniaxial stress–strain curve, where the strains are recoverable (elastic). Strength, defined by the yield stress at the onset of permanent (plastic) deformation or by the maximum strength at the peak load before fracture, is a measure of the force per unit area that the material can withstand. Hardness — another measure of strength — is estimated from the extent of penetration of an indenter into the surface of the material under an applied load. Ductility is a measure of the maximum strain before fracture, and is generally assessed as the per cent elongation of the sample or its relative change in cross-sectional area. Toughness measures resistance to fracture; it can be assessed in terms of the area under the load–displacement curve, but is better evaluated using the methodologies of fracture mechanics (see below).

Extrinsic versus intrinsic toughening

The attainment of both strength and toughness is a requirement for most structural materials; unfortunately, these properties are generally mutually exclusive[1]. Although the quest for stronger materials continues, they have little utility as bulk structural materials if they do not exhibit appropriate fracture resistance. It is materials with lower strength — and hence higher toughness — that find use in the most safety-critical applications, where failure is unacceptable. The development of such damage-tolerant materials has traditionally been a compromise between hardness and ductility, although there are alternative approaches based on the concept of extrinsic versus intrinsic toughening[129].

Lower-strength (ductile) materials develop toughness from the energy involved in plastic deformation. However, this cannot be used for brittle materials, which display little to no plasticity[1,130]. To toughen these materials, one must consider fracture as a mutual competition between intrinsic damage processes, which operate ahead of a crack tip to promote its propagation, and extrinsic crack-tip shielding mechanisms, which act mostly behind the crack tip to inhibit its propagation[129] (Fig. 3). Intrinsic toughening acts to inhibit damage mechanisms, such as cracking or debonding processes, and is primarily associated with plasticity (that is, the enlarging of the plastic zone); as such, it is effective against the initiation and propagation of cracks. With extrinsic toughening, the material's inherent fracture resistance is unchanged. Instead, mechanisms such as crack deflection and bridging[129] act principally on the wake of the crack to reduce (shield) the local stresses/strains experienced at the crack tip — stresses/strains that would otherwise be used to extend the crack. By operating principally in the crack wake, extrinsic mechanisms are only effective in resisting crack growth. Moreover, their effect is dependent on crack size. A consequence of this is the rising of crack-growth-resistance (R-curve) behaviour, where, due to enhanced extrinsic toughening in the wake of the crack, the required crack-driving force must be increased to maintain the subcritical extension of the crack. Natural structural materials display both classes of toughening, which is a major factor underlying their damage tolerance.

Fracture mechanics

To evaluate fracture resistance quantitatively, fracture mechanics is used. In linear elastic fracture mechanics (LEFM), the material is considered to be nominally elastic, with the plastic zone remaining small compared with the in-plane specimen dimensions. The local stresses, σ_{ij}, at distance r and angle θ from the tip of a crack, can be expressed (as $r \to 0$) by $\sigma_{ij} \to (K/(2\pi r)^{1/2})f_{ij}(\theta)$, where $f_{ij}(\theta)$ is an angular function of θ and K is the stress intensity, which is defined in terms of the applied stress, σ_{app}, crack length a and a geometry function Q. Hence the stress intensity, $K = Q\sigma_{app}(\pi a)^{1/2}$, represents the magnitude of the local stress (and displacement) fields[131]. Provided that K characterizes these fields over dimensions relevant to local fracture events, it is deemed to reach a critical value — the fracture toughness — at $K = K_c$ (ref. 132), provided that small-scale yielding prevails; for plane-strain conditions, the plastic zone must also be small compared with the thickness dimension. An equivalent approach involves the strain-energy release rate, G, which is defined as the rate of change in potential energy per unit increase in crack area. For linear elastic materials under mode I (tensile opening) conditions, G and K are simply related by $G = K^2/E$ (ref. 132).

LEFM-based measurements of toughness do not incorporate contributions from plastic deformation. Although many biological materials contain hard phases (for example, hydroxyapatite in bone or aragonite in nacre) that satisfy LEFM, they also comprise ductile or soft phases (such as collagen) that are a source of plasticity. When the extent of local plasticity is no longer small compared with the specimen dimensions, nonlinear elastic fracture mechanics (NLEFM) must be applied, whereby the crack-tip stress/strain fields are evaluated within the plastic (nonlinear elastic) zone. The field parameter J characterizes the local stresses/strains over dimensions comparable to the scale of local fracture events; the fracture toughness can be defined at the onset of fracture at $J = J_c$, where J is the nonlinear elastic equivalent of G in LEFM (ref. 133). Because of the equivalence of J and G, and in turn G and K, NLEFM enables the use of undersized specimens — too small to satisfy the stringent LEFM requirements — for measuring fracture toughness.

These toughness measurements are single-valued and pertain to where the initiation of cracking is synonymous with crack instability. In ductile materials, in many brittle materials toughened extrinsically and in most natural materials, fracture instability takes place well after crack initiation owing to the occurrence of subcritical cracking. To evaluate such crack-growth toughness, the R-curve can be used through the measurement of the crack-driving force (K, J or G) as a function of crack extension, Δa.

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(Box 2) — and translate them to other material combinations. Still, it is important to keep in mind that modern engineering demands that any bioinspired process must be scaled-up for practical manufacturing so as to accelerate fabrication and reduce the time between design and implementation. In fact, in this Review we contemplate whether the biomimetic approach for the creation of better structural materials will ultimately succeed. Our examination of this issue begins with a brief review of important natural structural materials and the mechanisms underlying their mechanical behaviour and function, and is followed by a detailed discussion of the key lessons offered by these materials and of the difficulties encountered in attempts to implement them in practical synthetic structures.

Structure and properties of natural materials

Biological materials are multifunctional. They combine biological, mechanical and other functions, and represent design solutions that are the local optimum for a given set of requirements and constraints. To separate mechanical from biological functions in natural materials, we derive material-property charts that represent sections through the multidimensional property space of materials and their performance[4] (Fig. 1a). Such charts usually show specific properties — that is, normalized by density — because when size or weight are not relevant constraints, one can more readily attain both high strength and stiffness in a material.

Almost all natural materials are composites of some form, comprising a relatively small number of polymeric (proteins or polysaccharides, for example) and ceramic (for instance, calcium salts or silica) components or building blocks, which are often composites themselves[3–7]. From this limited toolbox, an astonishing range of hybrid materials and structures are assembled. Wood, bamboo and palm, for example, comprise cellulose fibres within a lignin–hemicellulose matrix, shaped into hollow prismatic cells of varying wall thickness. Hair, nail, horn, wool, reptilian scales and hooves are formed from keratin, whereas insect cuticle consists of chitin in a protein matrix. The principal constituent of a mollusc shell is calcium carbonate, bonded with a few per cent of protein. Tooth enamel is composed of hydroxyapatite, and bone and antler are formed from hydroxyapatite and collagen. Collagen is the basic structural element for soft and hard tissues in animals, such as tendon, ligament, skin, fish scales, blood vessels, teeth, muscle and cartilage; in fact, the cornea of the eye is almost pure collagen[4].

When designing new materials, three factors are critical: chemical composition, nano/microstructure and architecture. Extensive manipulation of chemistry and microstructure is routinely required to make novel metallic alloys, ceramics, polymers and their composites. Throughout time, most advances in this area have occurred by trial-and-error experiments or through lucky accidents, as happened in the prehistoric Bronze Age and during its transition to the Iron Age. Conversely, evolutionary forces have led to the design concept of creating new materials with tailored properties through the manipulation of architecture, thereby permitting an enormous range of periodic, many-phase, continuous composites[8,9]. For

Box 2 | Common design motifs of natural structural materials.

Many natural materials must be equally light, strong, flexible and tough. Because such materials are built with a relatively limited number of components, it is not surprising that we can find common design themes among them.

Natural materials often combine stiff and soft components in hierarchical structures, as is the case for nacre, bone and silk. In many of these materials, the controlled unravelling of the soft phase during fracture acts as a toughening mechanism. It therefore seems that nature's hierarchical design approach is an effective path towards combining high strength and toughness. In contrast, man-made structural composites are still far from achieving the same degree of architectural control. For example, in mineralized natural structures (such as nacre, bone or enamel) the ceramic phase is often in the form of nanometre grains, nanoplatelets or nanofibres, all of which increase flaw tolerance and strength[128]. However, in synthetic ceramic nanocomposites (with the exception of nanozirconia-reinforced ceramics), the increase in strength is not usually accompanied by a significant increase in fracture resistance.

Structural materials found in nature use carefully engineered interfaces. At the nanometre level, the chemistry of the organic component is often engineered to template the nucleation and growth of the mineral phase. Despite recent advances in the mineralization of materials in the laboratory, we are still far from effectively using mineralization as a practical technique for the large-scale fabrication of bulk structural composites. In addition, interfaces in natural materials are also designed to avoid catastrophic failure at a large scale. Whereas in the laboratory the focus has been mostly on chemistry as a way to enhance interfacial adhesion, natural materials preferentially use topography to arrest crack propagation. Indeed, one can compare man-made technologies for hard coatings (those in cutting tools, for instance) with a natural equivalent (teeth). For instance, the enamel/dentin interface combines compositional gradients with scalloped interfaces, which ensures stability. Corrugated interfaces are also observed in fish armour[134]. Although there have been attempts to explore the effect of both topography and compositional and structural gradients[135,136] on the mechanical properties of man-made materials, we have yet to match the structural complexity of natural materials.

At the microscopic level, natural composites are usually complex and anisotropic. They can have layered, columnar or fibrous motifs. Quite often, the same structure can exhibit distinct layers with different motifs, such as the combination of columnar and lamellar regions in a shell. These motifs are usually orchestrated in sophisticated patterns, such as columns of circular layers in bone or wood, or the complex helicoidal arrangement of chitin fibres in the stomatopod club. Man-made composites can also be laminates or reinforced with complex fibre arrangements such as textile ceramic composites[137], but they have not yet attained the complexity of natural materials, which are characterized by features spanning many length scales.

Natural materials are often porous to provide paths for mass transport and/or to reduce weight. Furthermore, natural materials are usually graded or made of porous cores with dense shells to retain strength and flexibility. In some cases, such as bone osteons or dentin tubules, the pores play a significant role in toughening. Synthetic porous structures are usually crude in comparison; when high porosity is needed, it is usually at the expense of mechanical stability. The design of strong foams is now the subject of much investigation, and bioinspired hierarchical designs can offer efficient solutions[138].

Many natural materials are able to self-repair, often repeatedly and without external stimuli. In this regard, synthetic materials lag far behind. Although significant advances have been achieved in the area of self-healing structural composites, the number of repair cycles is often limited. To solve this problem, healing agents are delivered to the area of interest through vascular networks, or external stimuli (such as temperature) are used to trigger repair. There seems to be an inverse relationship between strength and the ability to repair autonomously multiple times.

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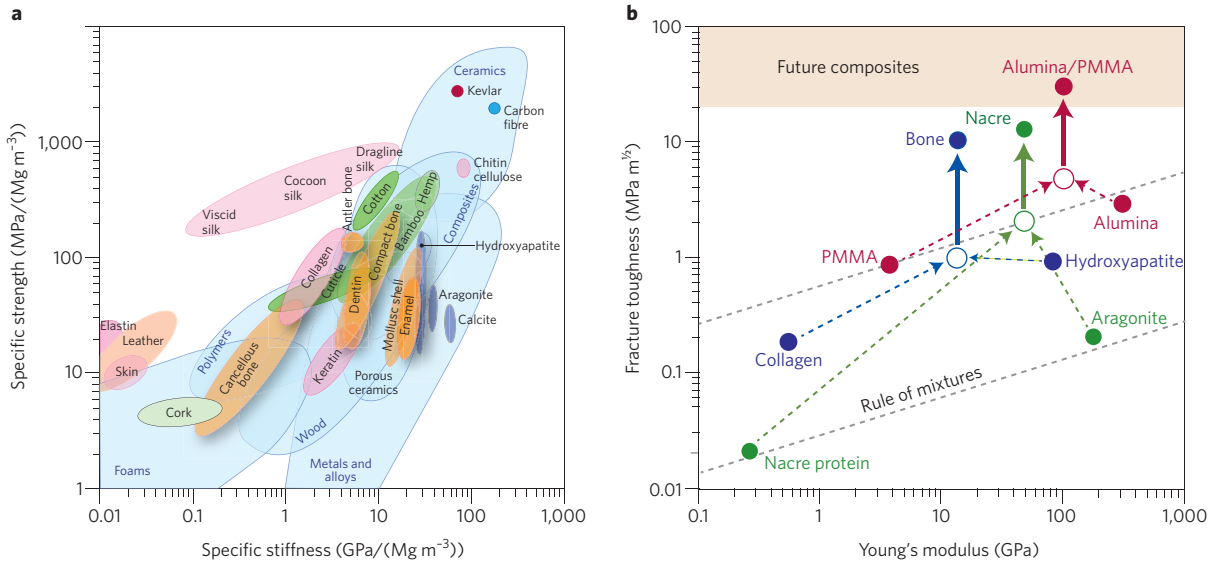

Figure 1 | Material-property chart, and projections for natural and synthetic materials. a, Ashby plot[4] of the specific values (that is, normalized by density) of strength and stiffness (or Young's modulus) for both natural and synthetic materials. Many engineering materials, particularly high-performance ceramics and metallic alloys, have values of strength and toughness that are much higher than those of the best natural materials. Silk stands out as an exception, sometimes reaching the extraordinary toughness of 1,000 MJ m^{-3} with a modulus of 10 GPa (ref. 122) — approaching that of Kevlar. One might therefore conclude that there is nothing spectacular about the properties of natural materials, as in general they seem similar to what can be made synthetically. However, quite unlike most synthetic materials, all natural structural materials use a limited chemical palette of inexpensive ingredients — typically, proteins, polysaccharides, calcites and aragonites, and rarely metals — whose properties are often meagre, and are formed at ambient temperatures with little energy requirements. Moreover, the constituents of natural materials are typically arranged in a hierarchical architecture of interwoven or interlocking structures that is difficult to reproduce synthetically. Many natural materials also repair themselves when damaged; in contrast, self-healing synthetic structures are still highly limited. **b**, Many natural composite materials, as exemplified by bone and nacre, have toughness values that far exceed those of their constituents and their homogeneous mixtures (as indicated by the dashed lines), and are able to sustain incipient cracking by utilizing extensive extrinsic toughening mechanisms (Figs 3 and 4b). This results in much higher toughness for crack growth (closed symbols above the solid arrows) than for crack initiation (open symbols), and thus higher fracture toughness (solid arrows). By mimicking the architecture of nacre in a synthetic ceramic material (alumina/PMMA)[85], similar behaviour and exceptional toughness can be attained.

example, if we consider bone and nacre, both of which comprise rather meagre constituents in terms of their mechanical properties, the resulting natural composites display far superior properties (as exemplified by their fracture toughness in Fig. 1b) that defeat the rule of mixtures. However, a pertinent question is whether we can emulate such designs and meet the greater challenge of making synthetic materials with such form and function.

One useful and frequently applied approach is that of materials design guided by first-principles calculations, which are based on an understanding of the different atomic components and the diverse sets of functional requirements. However, this strategy faces many issues. Despite decades of research, it has generally failed to yield significantly improved structural materials and performance, nor has it improved predictions of complex mechanical properties such as toughness[10]. One reason for this failure is that current computational capabilities and tools are insufficient to be able to integrate into one model physical mechanisms that act at multiple length scales and that affect a material's mechanical performance. Moreover, some natural materials, such as bone, have the capacity for healing, self-repair and adaptation to changes in mechanical usage patterns, which poses an even greater challenge for the engineering of materials that mimic natural structures.

Bone and nacre. As described in several recent review articles[11–15], bone and nacre (abalone shell) are prime examples of natural materials that combine strength with toughness, making them truly damage-tolerant. Also described in this subsection are other natural materials that have evolved efficient strategies for developing exceptional damage tolerance, including teeth, the dactyl clubs of stomatopod shrimps[16], and bamboo[17].

Bone is composed of cells embedded in an extracellular matrix, which is an ordered network assembled from two major nanophases: collagen fibrils made from type-I collagen molecules (~300 nm long, ~1.5 nm in diameter) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)) nanocrystals (plate-shaped, 50 nm × 25 nm in size, 1.5–4 nm thick) distributed along the collagen fibrils[18,19] (Fig. 2a). The hydroxyapatite nanocrystals are preferentially oriented with their *c* axis parallel to the collagen fibrils, and arranged in a periodic, staggered array along the fibrils[18,19]. These two nanophases make up about 95% of the dry weight of bone[18]. The structures form a tough yet lightweight, adaptive, self-healing and multifunctional material. Bone derives its resistance to fracture with a multitude of deformation and toughening mechanisms operating at many size scales, ranging from the nanoscale structure of its protein molecules to the macroscopic physiological scale[12].

The origins of fracture resistance in healthy human cortical bone can be conveniently separated into intrinsic mechanisms that promote ductility and extrinsic mechanisms that act to 'shield' a growing crack[12] (Fig. 3). Intrinsic toughening mechanisms result primarily from plasticity (Box 1). In bone, they originate from mechanisms at work at the smallest length scales, including molecular uncoiling of the mineralized collagen components and, most importantly, the process of fibrillar sliding. As load is applied, it is carried as tension in the mineral platelets and transferred between the platelets via shearing of the collagenous matrix[20]. This fibrillar sliding mechanism is essential to promote plasticity at this length scale. Many aspects of the collagen fibril's structure, such as the hydroxyapatite/collagen interface, intermolecular crosslinking and sacrificial bonding[21], play a role in its ability to promote fibrillar sliding efficiently. These features constrain molecular stretching and provide the basis

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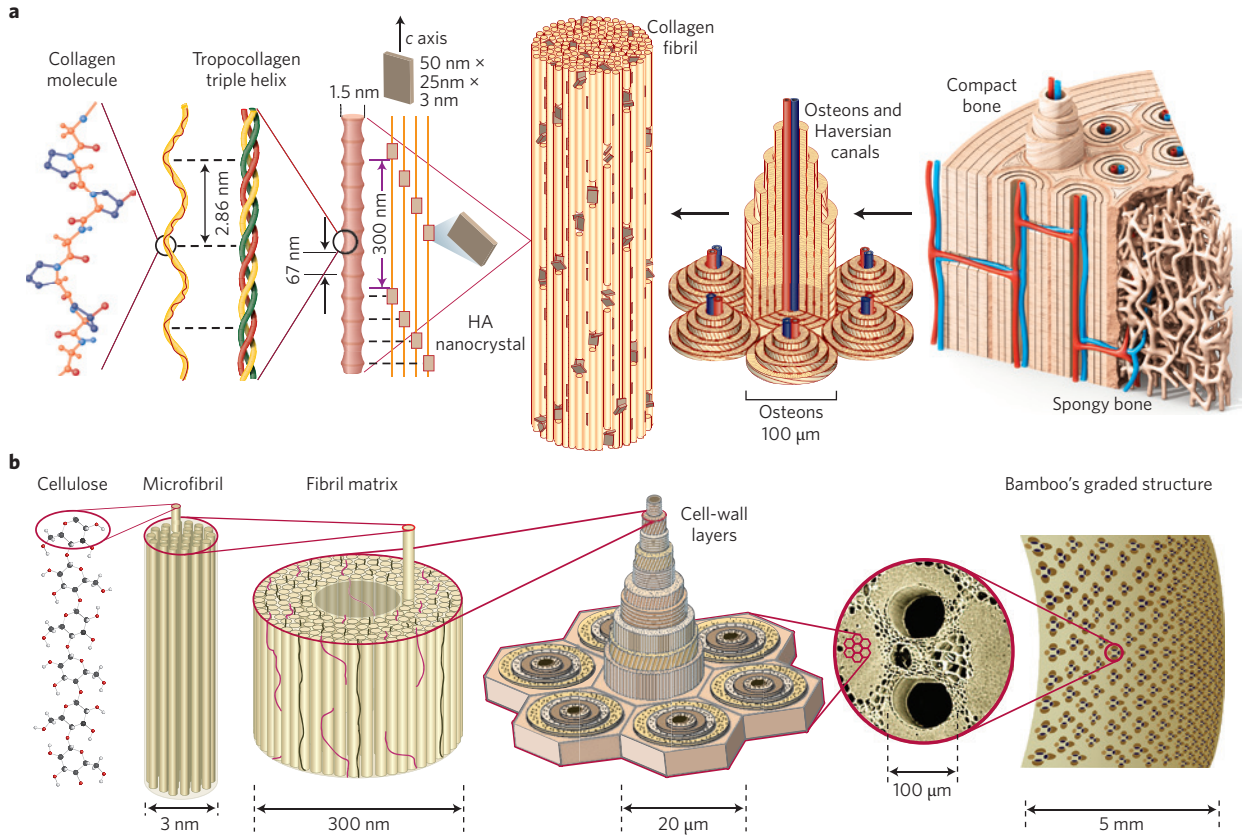

Figure 2 | Hierarchical structure of bone and bamboo. a, In bone, macroscale arrangements involve both compact/cortical bone at the surface and spongy/trabecular bone (foam-like material with ~100-μm-thick struts) in the interior. Compact bone is composed of osteons and Haversian canals, which surround blood vessels. Osteons have a lamellar structure, with individual lamella consisting of fibres arranged in geometrical patterns. The fibres comprise several mineralized collagen fibrils, composed of collagen protein molecules (tropocollagen) formed from three chains of amino acids and nanocrystals of hydroxyapatite (HA), and linked by an organic phase to form fibril arrays. **b**, Bamboo is composed of cellulose fibres imbedded in a lignin–hemicellulose matrix shaped into hollow prismatic cells of varying wall thickness. In bamboo and palm, which have a more complex structure than wood, a radial density gradient of parallel fibres in a matrix of honeycomb-like cells increases each material's flexural rigidity. Bamboo increases its flexural rigidity even further by combining a radial density gradient with a hollow-tube cross-sectional shape. Panel **a** adapted with permission from: right-most bone image, ref. 123, © 1995 by The Journal of Bone and Joint Surgery, Inc.; rest of panel, ref. 124, Nature Publishing Group.

for the increased strength of the collagen. This makes possible a large regime of dissipative deformation once plastic yielding has begun. As in most materials, plasticity and the resultant ductility provide a major contribution to the intrinsic toughness by dissipating energy and forming plastic zones surrounding incipient cracks, which further serves to blunt crack tips, thereby reducing the driving force for cracking.

However, an even larger contribution to the fracture resistance of bone arises from mechanisms of extrinsic toughening at coarser length scales, in the range of ~10–100 μm. Specifically, once the crack begins to grow, mechanisms within the microstructure are activated to inhibit further cracking; indeed, the primary drivers for this are the nature of the crack path and its interaction with the bone-matrix structure. Two salient toughening mechanisms can be identified[22,23]: crack bridging and crack deflection/twist (Fig. 3). Crack bridging occurs as microcracks form ahead of the crack tip, primarily along the hypermineralized interfaces at the boundary of the osteons, and producing the so-called uncracked-ligament bridges, which act as intact regions spanning the crack wake to inhibit its progress. Crack deflection is particularly potent in the transverse orientation, where cracks are aligned perpendicular to the osteons. As the crack begins to grow, structural features such as osteocyte lacunae and porosity can deflect the crack path. However, the largest features, specifically secondary osteons and in particular their brittle interfaces (cement lines), are most effective at crack deflection. Such crack deflection toughens normal bone by diverting the crack path from the plane of maximum tensile stress; as such, crack-tip stress intensity decreases (typically by a factor of two or more), and a larger applied force is required to propagate the crack further. Indeed, it is because of this that the fracture toughness of bone, which in the longitudinal direction is typically 1–5 MPa $m^{1/2}$, can be many times higher in the transverse direction, where cracks deflect at the cement lines. It is such extrinsic toughening (vertical arrows in Fig. 1b), resulting in increased resistance to both initiated and growing cracks, that is so effectively used in natural materials.

It should be noted that the small-scale intrinsic and larger-scale extrinsic processes are coupled. When the intrinsic toughness, generated at small length scales through fibrillar sliding, is degraded by biological factors (such as altered collagen crosslinking due to ageing and disease), the bone alternatively dissipates energy at higher length scales by microcracking. This is a form of plasticity that promotes extrinsic toughening at the microscale through the formation of deflected and bridged crack paths. Of course, a major characteristic of bone is its ability to remodel itself to repair damage — a trait that is difficult to replicate in synthetic materials. Indeed, there may be a coupling between bone inelasticity due to microcracking and the signalling that promotes such repair, as the microcracks are thought to severe the canaliculi, which are the means by which the osteocytes (osteoblasts that have become trapped within the bone matrix) remain in contact with other cells in bone.

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Whereas bone is an example of extreme structural complexity, nacre exhibits similar properties with elegant simplicity[15]. Essentially, both are laminated composites, containing hexagonal plates of either hydroxyapatite (bone) or aragonite (nacre; Fig. 4a–c). Nacre consists of 95 vol.% of layered aragonite ($CaCO_3$) platelets (~200–900 nm thick with a diameter of 5–8 μm), bonded by a thin (~10–50 nm thick) layer of organic material. However, its toughness is some three orders of magnitude higher than that of calcium carbonate[13]. Actually, the fracture toughness of aragonite is ~0.25 MPa $m^{1/2}$, whereas the toughness of nacre does not exceed 10 MPa $m^{1/2}$ (ref. 24), representing at best 40-fold increase in toughness (a factor of almost 2,000 in terms of energy).

The hard mineral aragonite provides for strength, but nacre would be brittle without a means of dissipating strain. Accordingly, inelastic deformation generated by limited interlayer shearing through the organic phase allows for such strain redistribution[25], thereby conferring toughness. The principal toughening mechanisms in nacre are crack bridging and the resulting 'pull-out' of mineral bricks — associated with controlled, yet limited, sliding of the aragonite layers over each other — and aided by viscoplastic energy dissipation in the organic layer (Fig. 4b,d). There is still debate regarding the mechanisms that restrain sliding. Among those considered are resistance from the lamellae nanoroughness[26], plastic deformation of the aragonite at the nanometre level[27], the organic layer acting as a viscoelastic glue[28], the presence of (pre-existing) mineral bridges[13,29], and, for certain nacres, platelet interlocking at the microscopic level[30]. As with bone, toughening in nacre is thus largely extrinsic and results in rising R-curve behaviour. The implication is that, unlike pure aragonite, a 95% aragonite composite material can tolerate the stable propagation of cracks.

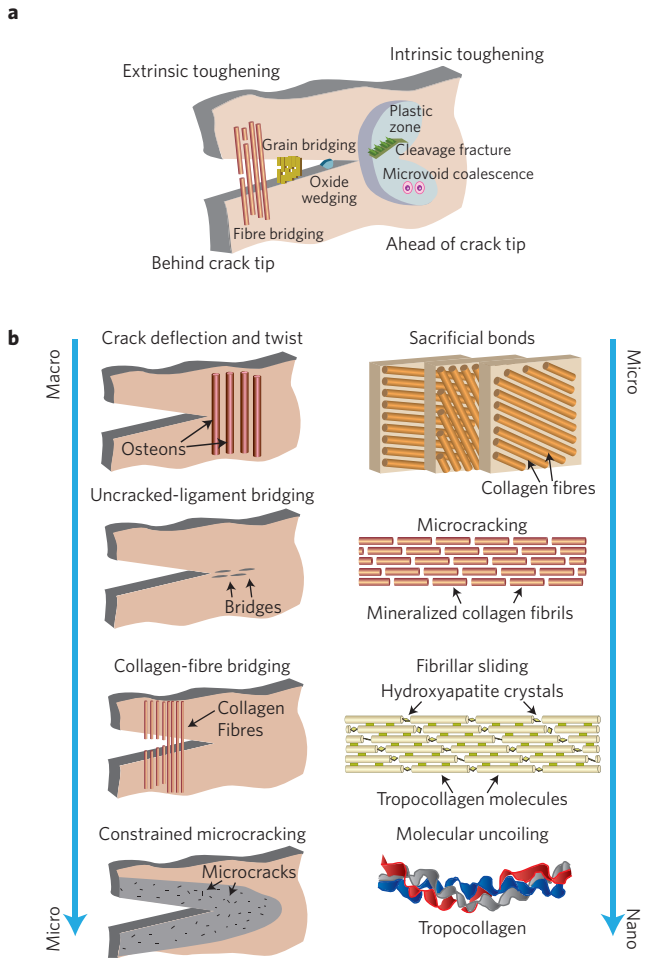

Figure 3 | Healthy human cortical bone resists fracture through complementary intrinsic and extrinsic contributions throughout its hierarchical structure. a, Intrinsic toughening mechanisms that promote plasticity occur ahead of the crack tip and act primarily at the nanoscale, whereas extrinsic toughening mechanisms, specifically those that shield local stresses or strains from promoting fracture, act at larger length scales and mostly behind the crack tip. **b**, Intrinsically, collagen fibrillar sliding is the prime plasticity mechanism in bone, and as such has the largest impact on the inherent resistance of the hydroxyapatite/collagen composite. Other mechanisms include molecular uncoiling, microcracking and sacrificial bonding, all of which operate at submicrometre length scales. Conversely, extrinsic mechanisms, such as uncracked-ligament bridging and crack deflection, occur at micrometre length scales once the crack begins to grow so as to shield the crack tip. Figure reproduced from ref. 12, 2010 Annual Reviews.

Because much research on bone and nacre has so far focused on structure-versus-property characterization as well as on how difficult it is to make synthetic materials in their image, it is easy to overlook that the making of these materials is the responsibility of cells. Indeed, the key to mimicking bone and nacre lies in understanding the involved cellular processes. However, many relevant biological issues remain unresolved. Both bone and nacre are soft–hard composites, and as such the roles of interfaces in the growth of these materials are crucial. Important steps in deciphering these roles have been the discovery of two new proteins that control the growth and crystal structure of aragonite[31], and how epithelial cells secrete all the necessary components for making the characteristic brick-and-mortar structure of nacre[32]. Further progress in discerning the underlying mechanisms that control these biomineralization processes should yield clues for the design of novel biomimetic materials.

Other natural structures (shrimp dactyl club, teeth, bamboo). Reports describing the special characteristics of many natural materials now appear on a regular basis. However, success in truly mimicking the structure and properties of these materials is still extremely limited — particularly if they must be processed in bulk form. Nevertheless, there has been significant progress in discerning some of the unique mechanisms. A case in point is a recent study on harlequin (peacock) mantis shrimp[16], which claimed that the dactyl club (biological hammer) of this creature has a much higher specific strength and toughness than those of any synthetic composite material[33]. In fact, the force generated by the club can reach 500 N, which is strong enough to break aquarium glass. These unusual properties and outstanding impact resistance are achieved by an elastic modulus mismatch that is controlled by the amount of mineral phase (crystalline and amorphous hydroxyapatite). The structure of the dactyl club consists of three distinct regions within an organic matrix, all comprising multiphase composites of oriented crystalline hydroxyapatite and amorphous calcium phosphate and carbonate. Each region has comparable thickness (~75 μm), separated by thin layers of protein (chitin). The resulting graded, layered structure, wherein each region has a different elastic modulus, forces any incipient cracks to continually change direction, thereby retarding crack growth via the extrinsic toughening mechanism of crack deflection.

Teeth. A product of 300 million years of evolution, teeth are among the oldest forms of tissue in mammals. Although teeth are frequently referred to as non-vital acellular structures, it should be noted that creatures with successful dentition survived, whereas those without it did not. Teeth are complex, graded structures consisting of enamel and dentin, supported in the jaw by connective tissues — cementum, periodontal ligament and alveolar bone. Enamel is extremely hard but brittle, with toughness as low as that of glass. Despite the fact that enamel is not a damage-tolerant material, it is able to withstand strong bite forces reaching 1,000 N, thousands

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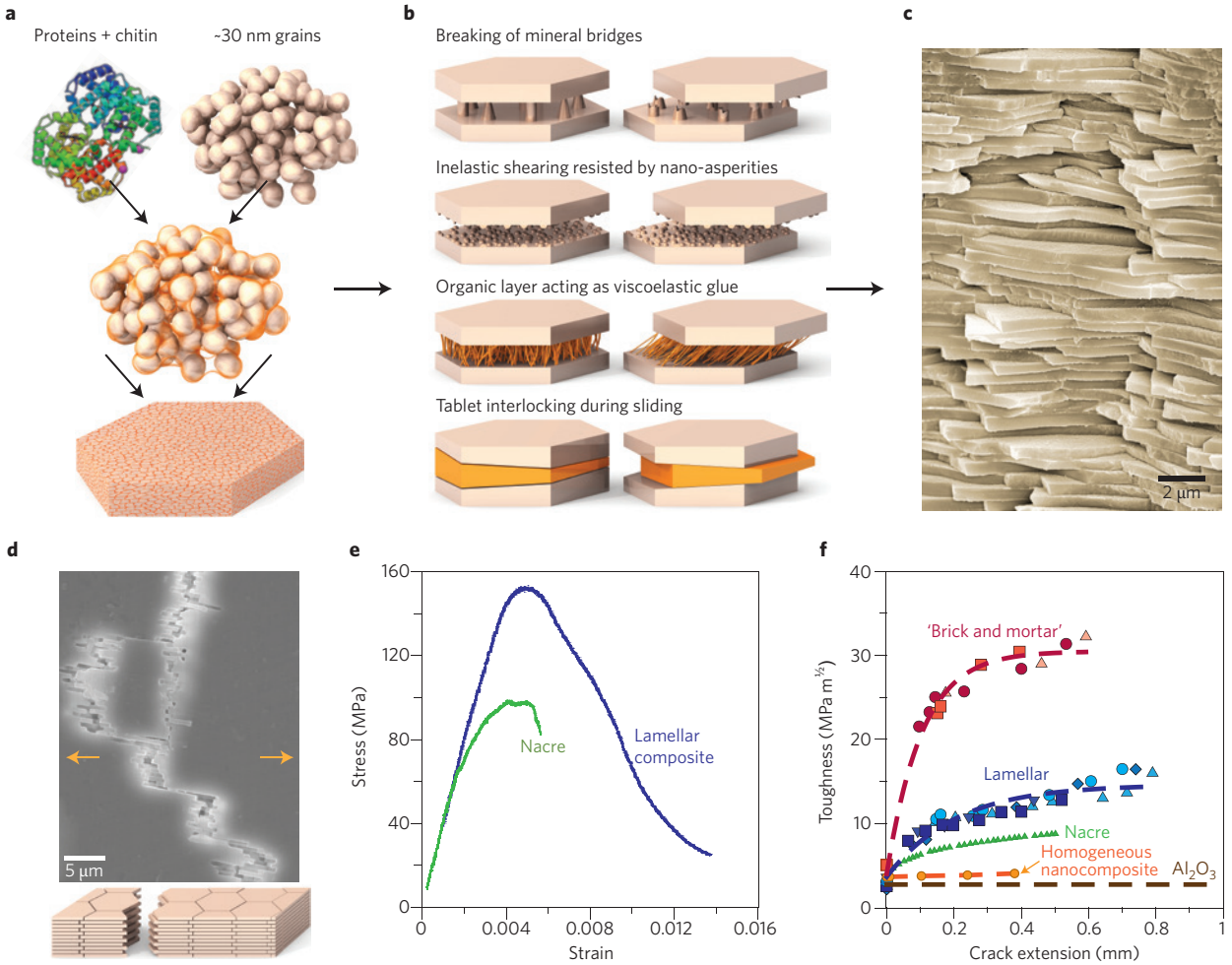

Figure 4 | The hierarchical structure and properties of nacre. a–d, Nacre is a brick-and-mortar structure (**c**) of $CaCO_3$ mineral platelets (aragonite), which provide strength, and proteins, which allow for ductility and toughness. The mineral bricks, which until recently were thought to be brittle single crystals, are ~500 nm thick and ~5–10 μm wide, and are comprised of millions of nanograins (~30 nm) glued together by a biopolymer[125] (**a**). If the platelets were rigidly interlocked, the resulting structure would be hard, yet hopelessly brittle. Instead, the biopolymeric mortar between the bricks generates limited deformation between the mineral layers (as shown by the mechanisms depicted in **b**), thereby allowing for the relief of locally high stresses while also providing ductility without too much loss in strength. Too much 'give' in the mortar, however, would result in lower strength; conversely, a mortar that is too hard would result in brick failure. Optimum properties come about when the strength of the mortar is fractionally less than the strength of the bricks, such that toughening through crack bridging can occur when the bricks pull out without breaking (**d**; orange arrows indicate the direction of tension). **e**,**f**, Comparison of the strength (**e**) and toughness (**f**) of natural nacre and nacre-like alumina/PMMA ceramics made using freeze casting[84,85]. Toughening is associated with brick pull-out and frictional sliding in the compliant polymeric layer. The nacre-like alumina/PMMA ceramic has exceptional fracture toughness, exceeding $K_c = 30$ MPa m$^{1/2}$, which is an order of magnitude higher than the toughness of its constituent phases and of homogeneous alumina/PMMA nanocomposites. Panels **e**,**f** reproduced with permission from ref. 85, © 2008 The American Association for the Advancement of Science.

of times per day[34]. It is therefore astonishing that, after millions of cycles, teeth are not failing more often due to mastication forces. As the dentin and enamel that make up teeth cannot repair damage and remodel like bone, how is that possible? The answer lies with the dentin tissue underneath enamel, which compensates for enamel's brittleness. The dentin–enamel junction (DEJ), known for its unique biomechanical properties, provides a crack-arrest barrier for flaws formed in brittle enamel[35]. The DEJ region is a complex mixture of enamel and dentin, where the enamel side is highly mineralized and the mantle dentin has more collagen, fewer tubules and less overall mineral than bulk dentin. Moreover, its structure is microscalloped (with concavities towards the enamel) to promote interfacial stability[36].

The underlying micromechanics that govern the structural resilience of teeth are well documented[34]. In simple terms, enamel is the hardest substance in the human body — comprising ~96 wt% mineral — and provides a tooth with a highly wear- and erosion-resistant surface layer. However, if the entire tooth was so constructed, it would readily fracture. The underlying dentin therefore has to provide a tough load-bearing base to accommodate excessive strains. This toughness, coupled with the crack-arrest characteristics of the DEJ, imparts fracture resistance to the tooth. The toughness of dentin is generated by its structure, which at the nanoscale is not so dissimilar to that of bone: it consists of a twisted matrix of mineralized collagen fibrils (~70% mineral, 20% organic, 10 wt% water). However, at the microscale, dentin is quite different: it is structured with an array of ~1-μm-diameter fluid-containing channels called dentinal tubules that radiate out from the pulp towards the exterior cementum, or the DEJ. The tubules have a thin cusp of mineral surrounding them that, under load, readily initiates microscopic cracks. Incipient cracks in dentin thus propagate into a 'sea of microcracks' that induces several potent extrinsic mechanisms of toughening.

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Because cracks always follow the more compliant phase, they are drawn to the tubules, thus resulting in tortuous and deflected crack paths, whereas the intact regions between the microcracks act as uncracked-ligament bridges[37]. The crack-arresting ability of the DEJ derives from similar phenomena: cracks from the enamel layer can actually penetrate the (optical) DEJ by ~5–10 μm, only to be arrested in the (mantle) dentin by the formation of crack-bridging ligaments[38]. It is noteworthy that these toughening mechanisms become less effective with age, thereby making teeth more prone to fracture. The tubules become filled with deposited nanocrystalline apatite, which makes them less effective stress concentrators and less susceptible to microcrack formation. Accordingly, growing cracks no longer follow the tubules, thus degrading both the crack-deflection and crack-bridging toughening mechanisms[39].

Bamboo and palm. Through optimization of their hierarchical architecture at each structural level, bamboo and palm achieve unusually high mechanical efficiency in terms of mechanical performance per unit weight[4,17,40,41]. Both are fibre-reinforced cellular materials in which the fibres are aligned parallel to the stem (in bamboo) or culm (in palm), forming an orthotropic composite. In contrast to wood, which has a comparatively homogeneous structure, the distribution of load-bearing fibres in bamboo and palm is not uniform, but rather creates a gradient of density and modulus, with fibre density being highest at the outer periphery, where the stresses are largest (Fig. 2b). Such graded structures significantly enhance the plant's flexural rigidity per unit mass (with mass being a measure of metabolic investment) as compared with that of a homogeneous distribution of the same number of fibres.

The exceptional structural efficiency of palm stems and bamboo culms derived from such property gradients is further associated with optimization of their cellular microstructure and tubular macroscopic shape[40]. A spruce stem with its cellular microstructure is twice as efficient as a stem of the same bending stiffness made from solid cell-wall material. The stems of the palms *Welfia* and *Iriartea* are ~1.5–2 times lighter because of the combination of a cellular microstructure with a property gradient. Moreover, bamboos are ~2–4 times more efficient than a beam with the same bending stiffness made from solid cell-wall material because they combine a cellular microstructure with a property gradient and a tubular shape. Wood, palm and bamboo are thus optimized to use the smallest quantity of the most highly efficient cell-wall material to perform their function. Does this mean that these plants are the global optimum among all possible designs? Probably not. What they achieve should instead be considered a local design optimum that, under a considerable number of constraints, allows the organism to perform both biological and mechanical functions to the best of its abilities[40,41].

Methods of processing hierarchical materials

The large span in length scales and the overall complexity of designing new biomimetic materials impose a combination of requirements and design motifs (Box 2) that are well beyond the reach of present technology. On the one hand, the basic knowledge required to meet these requirements is incomplete in many dimensions, in particular at the nanoscale. On the other hand, the need for novel processing routes to address multiple physical and mechanical factors imposes tremendous constraints on the choice of suitable materials. The ultimate objective is to develop smart materials that can both detect an event and structurally change in response to it. We are far from being able to achieve this goal today, but a concerted and well-directed effort may get us there within 10–20 years.

Biomimetic mineralization. All hard materials in animals (including humans) are mineralized from a limited number of inorganic components — calcium carbonate, silica (glass) and calcium phosphate being the most common. To build hard materials, living organisms take advantage of biomineralization, a process in which dedicated cells deposit minerals to a soft polymeric (protein) matrix to strengthen, harden and/or stiffen it. This shows that biomimetic mineralization could be, in principle, an obvious and effective process for building synthetic materials. However, the results reported so far are disappointing because the techniques are slow and only able to produce micrometre-sized specimens with mechanical properties that fall short of those of their natural counterparts[42–44]. In spite of this, the mineralization process has been used to grow particles, capsules and films with control of mineral morphology, size and even the crystalline phase[45–48]. The mineralization of an organic scaffold to create a practical three-dimensional (3D) material is particularly challenging. It requires a combination of the correct scaffold chemistry (to template mineral formation) with a suitable process that reproduces the role of cells[49–52]. The former is usually achieved by creating organic scaffolds with ion-binding sites that promote heterogeneous nucleation. Numerous strategies have been used, from the use of natural polymers — some of which are known to regulate mineralization in organisms[53,54] — to the application of phage display technologies to screen for optimum peptides that promote mineral nucleation[55], to the specific design of synthetic organic matrices[54,56–58]. Mineralization on carbon nanostructures, such as graphene or nanotubes, has also been investigated[59,60]. Mineral nucleation requires ion supersaturation, which can be reached, for example, through a controlled and homogeneous change in the pH of the solution in which the scaffold is immersed[61]. However, cells often promote localized mineralization using processes, such as the secretion of vesicles, that are difficult to replicate in the laboratory[2,62]. Furthermore, although much work has focused on the control of mineral growth and structure at the nanoscale, manufacturing techniques that use biomimetic mineralization for fabricating complex composites with features ranging from the micro- to the macroscale (as required for structural applications) are still far from being practical.

An intriguing approach for the formation of complex structures with several organization hierarchies is the combination of controlled mineral growth and subsequent particle self-assembly following external stimuli[63,64]. In this approach, smart responsive particles are prepared through functionalization by using either inorganic nanoparticles or organic molecules. External stimuli can then be used to control the assembly of the functionalized particles or their distribution within a composite. For instance, it has been demonstrated how functionalization with organic molecules can be used to promote recognition and self-assembly so as to build ordered structures[65]. Janus particles — particles that display different chemistry on opposite sides of their surface — can be used to obtain complex hierarchical arrangements[66]. Progressing from particle assembly at the nanoscale and microscale to making a practical structural material still represents a major problem, although there have been some significant advances. For example, magnetic fields can be used to control the distribution of a magnetic reinforcement in a polymer[67]. By using magnetic fields on ceramic platelets functionalized with magnetic nanoparticles at their surface, composites with complex arrangements of these platelets within an organic matrix have not only been made with practical dimensions, but also manipulated to achieve a desired mechanical response[68]. It has also been possible to create macroscopic structures using particles that can assemble in emulsions[69,70]. In some cases, this assembly was made reversible by functionalizing the particles with pH-responsive polymers[69]. However, the extent to which it is possible to mimic natural structures using these techniques is still a matter of debate.

Nacre-like composites. The remarkable damage tolerance of nacre's brick-and-mortar structure seems to be deceptively simple and easy to emulate[5,71]. However, the sobering fact is that at present there are no processing techniques that can make composites with

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a comparably high mineral content. Also, conventional processing techniques, such as slip/tape casting combined with hot pressing, reaction sintering and chemical vapour infiltration, cannot provide the degree of microstructural control down to the nanoscale that is needed to manipulate and optimize the mechanical response of the material. A possible alternative would be to build a complex macroscopic structure through controlled assembly of atomic- or nanometre-sized blocks and with controlled precipitation of mineral phases (as in natural nacre), but this has yet to be realized. Indeed, most bottom-up fabrication techniques are limited to thin films or micrometre-sized samples. Largely because of these difficulties in processing, we are still awaiting the successful production of biomimetic structural materials in bulk.

Another key issue concerns the fact that mineralized biological composites, in particular bone, dentin and nacre[23,72], generate fracture resistance primarily by extrinsic toughening mechanisms that shield cracks from applied loads. These mechanisms, which are different from those that toughen metals, span so many dimensions that they are often difficult to replicate in a synthetic material. Moreover, we do not yet completely understand how the diverse structural features that act at multiple length scales interact to generate simultaneously the desired mechanical properties and biological responses.

Numerous processing techniques have been proposed to produce nacre-like materials, and several outstanding examples of biomimetic organic/inorganic materials have been fabricated using layer-by-layer deposition[73–76], solution casting[77], self-assembly[49,78] and thin-film or tape deposition[79]. However, these processes have often been limited to the making of a few thick (~200 μm) ceramic layers that are not yet suitable for structural applications or that cannot replicate all the nuances of the natural counterpart.

A recent review article of nacre processing techniques concluded that many of the current techniques are not feasible for practical materials production[80]. Still, we believe that freeze-casting, hot-press-assisted slip casting, electrophoretic deposition and paper-making methods all have potential. Of these, freeze casting and hot-press-assisted slip casting are probably the best-suited techniques to produce bulk material.

The notion of making a nacre-like material — hard composite 'bricks' interspersed with soft 'mortar' layers — is simple in principle, but extremely difficult in reality. First, there is a need to tailor features to achieve optimal properties. For example, 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. Also, the alignment, shape and roughness of the bricks must be perfected, and this is not easy to accomplish. Hence, successfully produced biomimetic nacre requires the design of optimum microstructures and the development of fabrication procedures that can implement such microstructural designs[81]. One of the first examples of the development of bulk nacre-like composites, reported in 1990, utilized SiC ceramic tablets coated with graphite to provide weak glue-like interfaces[82]. A decade later, a combination of extrusion, roll compaction and hot-pressing techniques was employed to create nacre-like (and bamboo) composites from Si_3N_4 instead of SiC, an interlayer of BN instead of carbon[83], and with SiC whiskers added to the Si_3N_4 matrix, and Al_2O_3 and Si_3N_4 to the interlayer, so as to improve, respectively, strength and adhesion. The resulting fibrous monolithic composites displayed a fracture toughness of 24 MPa $m^{1/2}$, yet at the expense of decreased composite strength.

Freeze casting. A more recent attempt at mimicking nacre in a bulk material involved the use of freeze casting (also known as ice templating) to provide a new class of bioinspired ceramic materials with exceedingly high toughness[84,85]. This technique is a relatively

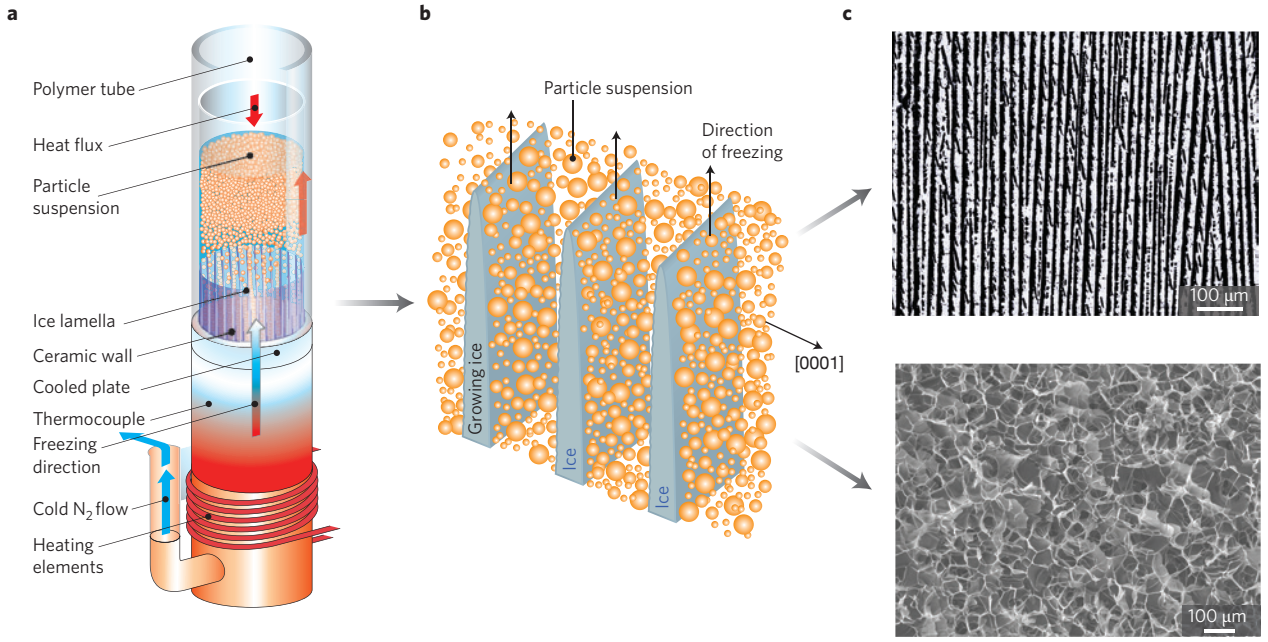

Figure 5 | Processing of nacre-like structures by freeze casting. a, Freeze casting uses both the directional freezing of, generally, ceramic suspensions and the microstructure of ice to template the architecture of scaffolds, and thus can be used to create porous, layered materials[84,126,127]. **b**,**c**, Controlled freezing results in the formation of lamellar ice crystals that expel the particles and/or dissolved molecules as they grow. The particles accumulate in the space between the crystals, leading to the formation of a lamellar material (exemplified by the freeze-cast lamellar alumina (top) and porous chitosan (bottom) micrographs in **c**) after the ice has been sublimated by freeze drying and the material has been sintered. Particles trapped by the ice crystals form bridges between lamellae, and these bridges make a critical contribution to the mechanical properties of the layered material. The relevant microstructural dimensions — pore and lamellae widths and wavelengths from one to hundreds of micrometres — can be controlled by adjusting the composition of the suspension (solid content and solvent formulation) and the speed at which the ice grows. Figures adapted with permission from: **a**, ref. 126, 2010 The Royal Society; **b**, ref. 127, © 2006 Acta Materialia Inc.

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inexpensive procedure for the controlled freezing of ceramic-based suspensions in water, and as such provides a means to mimic natural structural designs over several length scales. Specifically, ceramic suspensions are directionally frozen under conditions designed to promote the formation of lamellar ice crystals, which expel the ceramic particles as they grow (Fig. 5a,b). After sublimation of the water, this results in a layered homogeneous ceramic scaffold that, architecturally, is a negative replica of the ice. The scaffold can then be filled with a second soft phase so as to create a hard–soft layered composite. It is also possible to create brick-and-mortar structures by compressing the layered ceramic scaffolds before the introduction of the soft phase[84]. Also, by controlling the freezing kinetics and the composition of the suspension, the architecture of the material can be adjusted at several length scales so as to replicate some of the microstructural features responsible for the unique mechanical response of like-nacre materials. Furthermore, the thickness of the lamellae can be manipulated by controlling the speed of the freezing front, such that materials with lamellae as thin as 1 μm (close to that of nacre) ordered over macroscopic dimensions can be fabricated in practical sizes (Fig. 5c). The roughness of the lamellae (which replicates that of the ice crystals) can be engineered at submicrometre to micrometre levels by using additives such as sucrose, salts or ethanol, which vary the solid–liquid interfacial tension and the phase diagram of the solvent. Moreover, the growing ice crystals can split and trap ceramic particles, which generate inorganic bridges between lamellae. All of these factors, together with the roughness of the ceramic, the properties of the soft phase and the strength of the hard/soft interface, control how much the ceramic bricks can slide relative to each other, which, as with natural nacre, is the dominant mechanism controlling the ductility of the material.

Freeze casting has been used to fabricate metal/ceramic and model polymer/ceramic (poly(methyl methacrylate); PMMA)/alumina and, more recently, PMMA/SiC hybrid materials with fine lamellar or brick-and-mortar architectures — the latter with high ceramic contents up to 80 vol.% (refs 84–87). In these cases, the objective was to allow for stress relaxation by combining a strong and hard (ceramic) phase with a compliant (polymer or metal) layer in between. The nacre-like PMMA/alumina materials in particular showed remarkable R-curve behaviour, thus indicating that they are tolerant to the stable growth of cracks, with a fracture toughness of 30 MPa $m^{1/2}$ or more and yield strengths of 200 MPa (some 300 times higher in energy terms than those of either the constituent ceramic or polymer[84,85]; Fig. 4e,f). Furthermore, they were shown to be 50–100% more ductile than nacre, and twice as strong. In fact, such hybrid alumina ceramics approach the specific strength and toughness of aluminium metal alloys while exhibiting lower density and higher stiffness. Strong and tough ceramics have also been fabricated through the freeze casting of platelet-containing suspensions[88], which opens new questions regarding the role of the soft phase in nacre-like materials[89].

Freeze casting can also be used for making efficient cellular structures. Although foaming techniques are well established, freeze casting and 3D printing both offer many advantages in creating such structures. For example, directional solidification during freeze casting of platelet-based slurries can be used 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 platelets during processing[90].

Additive manufacturing. This type of manufacturing encompasses a family of technologies that draw on computer designs to build structures layer by layer. Different approaches have been developed, such as droplet delivery (typically, 3D inkjet printing), continuous extrusion (for example, robocasting), selective laser sintering, and the use of light to cure designed areas in polymer-containing suspensions (for instance, stereolithography or two-photon polymerization). Additive-manufacturing technologies have been used to build functional networks of cellular materials and complex devices such as batteries, photonic crystals, tissue-engineering scaffolds, catalyst supports and foams for acoustic-, vibration- or shock-energy-damping applications.

In some respects, it may be ideal to use additive manufacturing to assemble, on demand, structures modelled after natural materials[91–94] (Fig. 6). However, the practical fabrication of bioinspired composites with these techniques will hinge on the ability to solve some difficult problems. First, the palette of materials that can be processed by additive manufacturing ought to be broadened. Only a number of metals, polymers and in particular a limited number of ceramics can now be used to build structures with features ranging in size from tens of micrometres to one submicrometre, depending on the technology. In fact, the high thermal stability of ceramics in part hampers the use of techniques that involve melting or *in situ* sintering. Most ceramic additive-manufacturing technologies require an 'ink', typically a colloidal suspension in water or other solvent, or a wax containing ceramic particles[95,96]. Furthermore, the parts usually require additional thermal treatments for consolidation. To make things more complicated, bioinspired materials are usually hybrids that combine dissimilar materials (for example, a polymer and a ceramic) — something that may be difficult to construct using a single technique.

Second, the precision required to print nanoscale features ought to be combined with the fabrication of large-scale components. On the one hand, continuous extrusion of sol–gel ceramic inks[97], two-photon polymerization (nanolithography)[98] or inkjet printing[99] can be used to build materials with fine features; however, they cannot be used to create large structures. On the other hand, techniques such as robocasting using colloidal ceramic inks, 3D printing or stereolithography[95,100,101] offer the potential for large-scale manufacturing, yet their ultimate feature resolution is of the order of tens or hundreds of micrometres.

Despite these difficulties, there has been some progress. For example, recent studies have demonstrated that tissue constructs that mimic living tissue can be made by printing tens of thousands of picolitre droplets in 3D[102]. Also, additive manufacturing has been used to fabricate model structures inspired by natural composites, such as nacre or the stomatopod club[30,103]. Although the characteristic features of such model composites are usually orders of magnitude larger than in their natural counterparts, they provide a powerful platform for isolating and testing a specific design concept taken from nature.

Additive manufacturing may provide a path towards fabricating the bioinspired structural materials of the future. Much work is still needed, particularly because the current 'Achilles heel' of such techniques is the difficulty of controlling the surface quality and microstructure of individual layers and segments, thus hampering the reliable combination of mechanical properties required for the structural application of the finished materials[104–106].

Looking ahead

After decades of research, it seems that many structural materials are quickly approaching their performance limits. For example, Ni-based superalloys in jet-engine gas turbines have reached their temperature ceiling. Additionally, there is an unmet demand for lighter, tougher and more wear-resistant materials across a range of applications, from minimally invasive orthopaedic implants to high-efficiency industrial cutting and drilling tools. Where do we go from here? What will inspire new ideas? Bioinspired design clearly provides one feasible route. In the natural world, multiple-scale, multifunctional and hierarchically organized structures result in hybrid materials with unusual, often remarkable, properties acquired through combinations of relatively mundane constituents. Although we can draw on natural materials themselves for use

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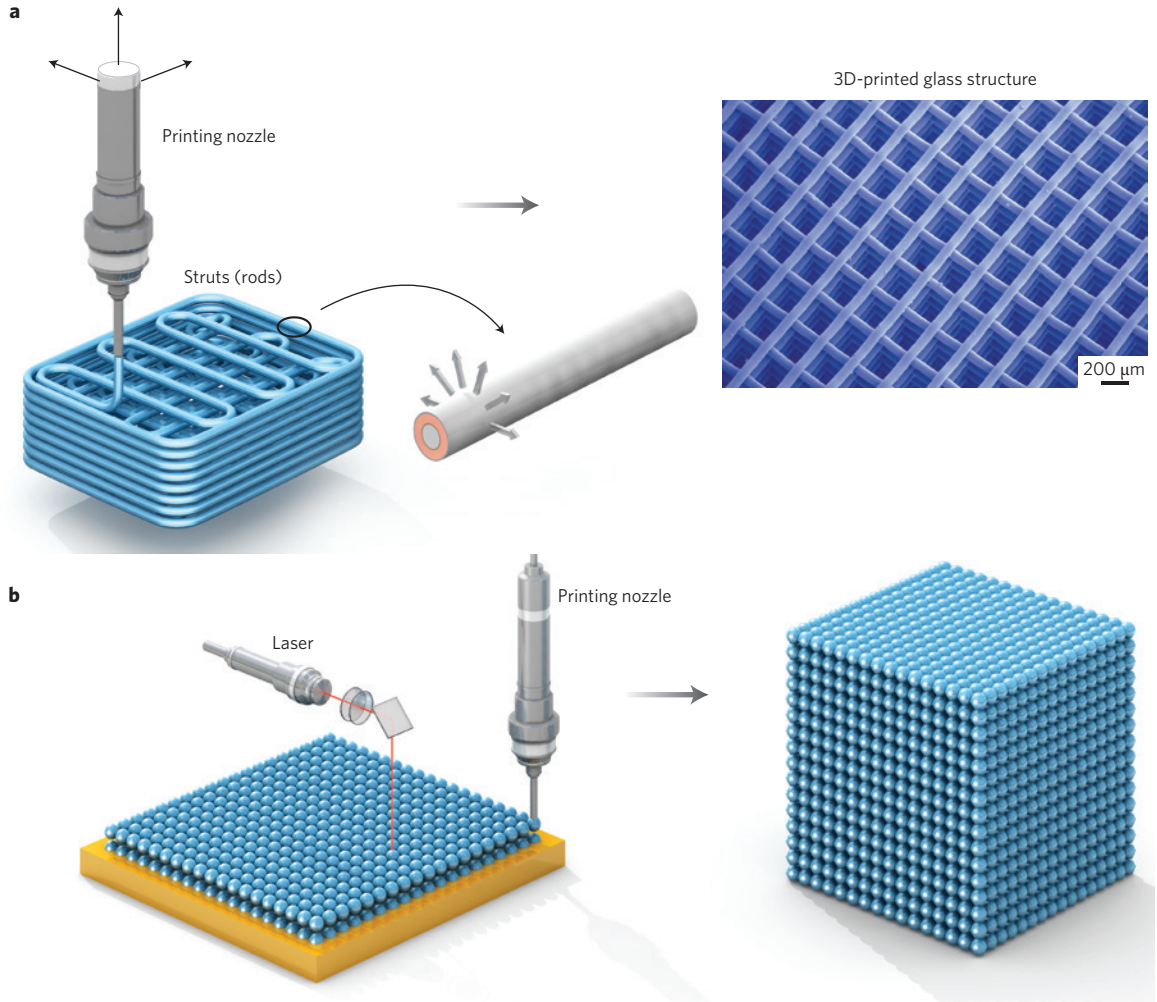

Figure 6 | Additive-manufacturing techniques. a,**b**, Custom-designed solid materials with complex architectures can be precisely and reproducibly fabricated through free-form additive-manufacturing processes (3D printing). These include direct inkjet writing and robotic-assisted deposition (robocasting), which can generate, for example, glass 3D-printed scaffolds (**a**), as well as droplet-deposition (jetting), to form, for instance, printed droplet networks (**b**). Jetting represents a promising platform for the manufacturing of complex functional devices[102]. These techniques usually involve the layer-by-layer printing of structures generated by computer-aided design or obtained from image sources, such as magnetic resonance imaging. Simultaneously with droplet deposition, a laser pulse can be used to induce the vapourization of organic solvents, the fast sintering of metal and ceramic droplets, or the polymerization of a composite structure.

in applications at ambient conditions, the challenge is to translate insights gained from observing their complex architecture into structural materials that can operate under extreme environments, in ever increasing temperatures and pressures. Another noteworthy observation is that natural structures are usually optimized for specific applications. The microstructure of enamel, for instance, varies from animal to animal or even from tooth to tooth. However, synthetic materials usually see a wider range of applications. Aerospace alloys, for example, are also used in orthopaedic implants. Will bioinspired synthetic materials also become highly specialized? If so, economic considerations are likely to become as important as performance.

In basic terms, there are two fundamental challenges facing researchers in the field of bioinspired materials: (1) to devise approaches for translating design motifs found in natural materials to a wider range of material combinations; and (2) to create methods for making bioinspired structural materials in practical form and in bulk.

The first of these challenges is exceedingly complicated. For example, can the complex role of nacre's protein film be captured by a thin metal or carbon layer? Whereas the soft components in materials such as nacre or silk are built of molecules designed to unravel in a controlled manner so as to accommodate significant deformations, the thin, confined metallic layers may exhibit fairly limited plastic deformation. It has thus been suggested that nanoporous ceramic interlayers can be used to replicate the role of the protein layer in nacre[89], and recent work shows how high fracture resistance can be achieved in glass by guiding the crack path through interlocking interfaces without the addition of soft phases[107]. The translation of natural design motifs will therefore require a deep understanding of the mechanical behaviour of materials and interfaces in volumes down to the nanoscale. This is an area of research that has attracted much interest in recent years[108–110], but we are still far from understanding how natural materials are built or develop their properties. In this respect, the inherent hierarchical nature of biological materials demands new multiscale modelling approaches to capture fully the relationship between structure and performance. This is a relatively new field that is already yielding much insight into, for example, the parameters that control the behaviour of brick-and-mortar structures. Indeed, the nature of the adhesion at the hard/soft interface, as well as the structure of the bricks and the properties of the mortar[30,89,111–116], have been recently explored.

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The second challenge is primarily focused on manufacturing. New processing techniques, such as those reviewed here, undoubtedly offer much early promise, yet more effort must be devoted to them before their potential can be realized. Integrated computational modelling of both the manufacturing process and resultant properties will be important[117], despite the fact that the ability of these techniques to predict critical mechanical properties, in particular fracture toughness, fatigue or wear resistance, is still a long way off. The key feature responsible for the success of natural materials is the precise way in which their components are arranged in space (architecture) across numerous length scales. The natural world provides us with a blueprint to emulate, yet we must develop our own methods of construction. The synthesis of nacre-like or bone-like materials is an attractive goal, but we have yet to demonstrate a system that is sufficiently durable or can be manufactured at a reasonable cost. Furthermore, it is possible that the term 'bioinspired' is being abused. Many layered materials available to engineers today are quite far from the structure of nacre, and not all porous foams imitate the architecture of bone or wood. The development of practical manufacturing approaches is further off than many researchers would like to believe.

A common theme when reviewing current processing technologies is the lack of systematic methodology for dealing with the structural complexity of a truly bioinspired structure whose dimensions span from the nanoscale to the macroscale. Traditional materials science has focused on the microscale; more recently, nanotechnology has opened new opportunities. However, it remains a dauntingly complex problem to develop a manufacturing technique that will allow flexible control of nanometric features in structures built at large scales. One solution is to combine two or more fabrication technologies. For example, can 3D-printing techniques be used to build scaffolds that can be subsequently mineralized? An example of this is the combination of solid free-form fabrication with thin-film deposition techniques to create ultralightweight metallic and ceramic microlattices; in fact, initial studies have demonstrated that significant improvements in mechanical efficiency can be achieved[118,119]. An alternative solution is to apply a reductionist strategy: to fabricate large-scale structural components through the controlled assembly of small building blocks or modules. These can be defined as homogeneous and viable constructs, built with nanometre-level precision using existing techniques, and with surfaces that are specifically engineered to interconnect in a tightly controlled manner and provide specific functions. Using such modules, complex hierarchical structures can be built from simple units, and complex processes can be orchestrated that mimic strategies by which natural materials are assembled from smaller modules, each designed to perform specific functions.

Beyond their passive mechanical response, natural structures are active in that they respond and react autonomously to external conditions, and are able to self-repair, often repeatedly. Although these possibilities are outside the scope of this Review, scientists and engineers are already researching ways to replicate these traits in engineered composites, from the use of microvascular networks to deliver healing agents[120], to the design of self-shaping composites[121].

Natural structures are wonderful examples of what can be done with a fairly limited selection of materials. Humans have enriched the natural-materials palette with thousands of synthetic compounds. Perhaps because there is such an abundance of synthetic materials, we have not been compelled to refine their designed architectures with the same degree of sophistication. Compared with the complexity of natural materials, many synthetic materials may in fact seem crude. With the advantage of time, natural evolution has led to nano- and microstructures as advanced and sophisticated as the large-scale designs of bridges or buildings. Bioinspiration thus poses a simple and enticing challenge: how far can we go in manipulating structure? This is not just a test of human ingenuity; the potential pay-out is huge. The possibility of marrying the structural control found in nature with the huge variety of synthetic compounds could lead to the development of new materials, extend the range of application of current ones, and break existing limitations in terms of weight, toughness, strength and environmental resistance. Attaining those goals would be a major technological advance. In the end, regardless of whether bioinspired materials are widely implemented, even those sceptical of their promise must recognize that understanding natural structures and finding ways to replicate them will yield insights that can drive materials science forward for years to come.

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Author contributions

All authors contributed equally to this work.

Additional information

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Competing financial interests

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