

## Biological materials by design

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## Topical Review

# Biological materials by design

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## Abstract

In this topical review we discuss recent advances in the use of physical insight into the way biological materials function, to design novel engineered materials ‘from scratch’, or from the level of fundamental building blocks upwards and by using computational multiscale methods that link chemistry to material function. We present studies that connect advances in multiscale hierarchical material structuring with material synthesis and testing, review case studies of wood and other biological materials, and illustrate how engineered fiber composites and bulk materials are designed, modeled, and then synthesized and tested experimentally. The integration of experiment and simulation in multiscale design opens new avenues to explore the physics of materials from a fundamental perspective, and using complementary strengths from models and empirical techniques. Recent developments in this field illustrate a new paradigm by which complex material functionality is achieved through hierarchical structuring in spite of simple material constituents.

Keywords: materials, bio-inspired, mechanical properties, simulation, experiment

(Some figures may appear in colour only in the online journal)

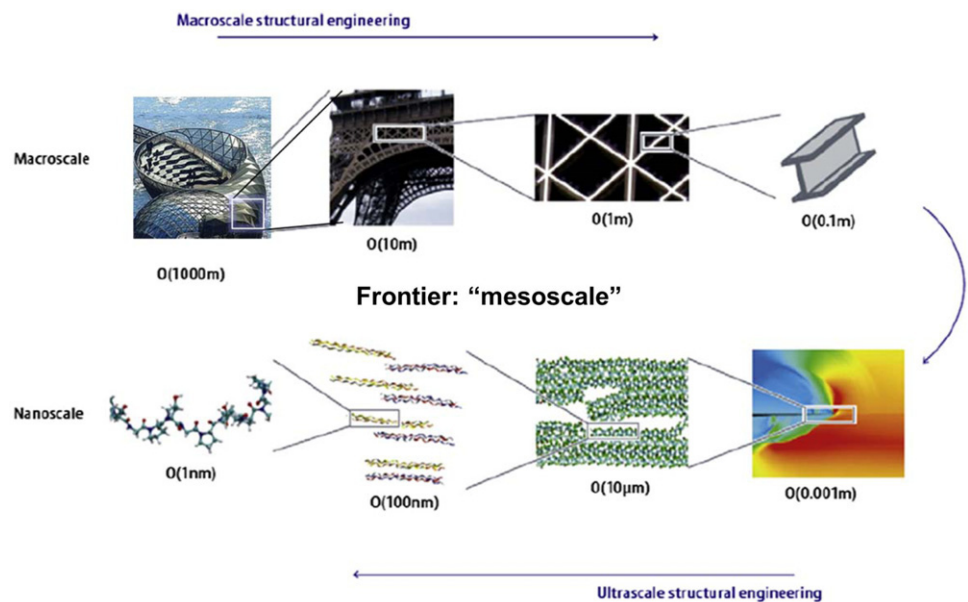
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## 1. Introduction

Biological material covers a range of materials that are expressed by genetic information and play functional roles for the biological system such as bone, silk, and wood [2]. These

materials have fascinating mechanical and biological functions built up from simple basic material building blocks (figure 1) [3]. They are mostly constructed from self-assembly, which is based on their chemical constitution and requires low energy input. Such ability to integrate multiple advantages in materials goes beyond our current capacity in designing and synthesizing engineered materials. It is worthwhile learning how biological materials are constructed and applying the knowledge in advanced manufacturing, to realize materials by design, from a concept to a computer model, to optimization, and realization of a physical specimen. One major obstacle hindering us in applying these concepts in engineering is that the underlying mechanisms remain largely obscure, in particular, including how molecules are synergistically organized at different length and time scales to form the macroscopic material [2, 4–6]. Recent advances in nanotechnology and multiscale computational tools, combined with transformative ways of synthesizing materials and structures, now provide appropriate approaches to bring that hidden knowledge to light [7]. We have developed an increasingly improved ability to investigate structures and properties through all scales from



**Figure 1.** Grand challenge of hierarchical material design by controlling all length scales in concept, design and modeling, optimization, and manufacturing. The massive manufacturing approaches used in the 19th and 20th centuries are being replaced by highly flexible dedicated methods that increasingly mimic natural processes—such as grown materials, molecular-based design, and enhanced degrees of personalization and diversification of features. Figure adapted from [1].

**Table 1.** How to make materials: a summary of different manufacturing techniques at different characteristic length scales, and associated examples.

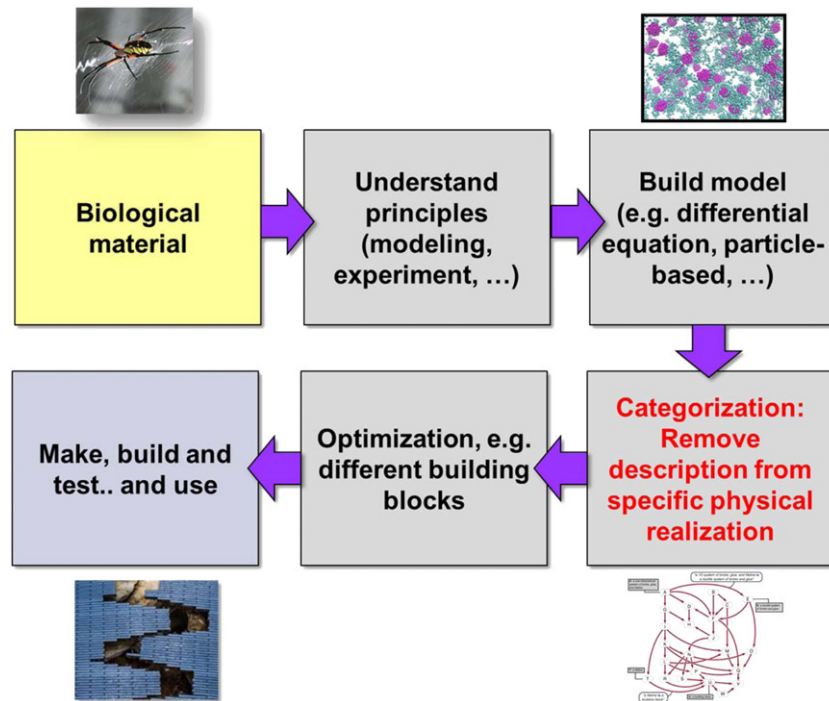
Technique	Physical mechanism	Length-scale	Example
Protein folding	Chemical (charges, hydrophobic effects, etc)	Angstroms to nanometers	Elastin, collagen
Self-assembly	Chemical, geometrical	Angstroms to micrometers	DNA origami, Amyloid biofilm
Fluidic flow	Physical forces (elongation, shear, etc)	Tens of nanometers to millimeters	Spider silk spinning duct, microfluidic device for drug delivery
Additive manufacturing	Digital casting Photochemical reaction	Tens of micrometers to millimeters	3D printing
Conventional manufacturing	Material solidify and solid fracture	Micrometers to kilometers	Molding and cutting

nanoscopic to macroscopic, and to elucidate the full blueprint for reverse engineering the structure–property relationships of these materials, as shown by the manufacturing techniques summarized in table 1.

Indeed, we are beginning to be able to investigate and build biological and biologically inspired materials in a systematical way. Critical advances in a number of scientific fields have the potential to revolutionize how we design, analyze, and make materials and structures (figure 2). By performing comparative bottom-up analysis of biological materials using multiscale computational methods, and exploiting advances in basic concepts of physics and chemistry, a comprehensive description can now be achieved, allowing for a systematic classification of the various mechanisms that occur in different materials, and enabling the translation from natural to synthetic materials [6, 8]. The application of tools from statistical physics, advanced mathematics, and new computational methods can be

used to extract useful information from a very large database with the help of supercomputers and relevant algorithms. We can categorize a material as a set of interacting elements that are conceptually represented as a graph, forming an abstract way to show how a material works [8].

In this topical review, we discuss recent advances that use physical insight into how biological materials function, and how these are used to use the knowledge in synthesizing new materials. To illustrate the basic concepts we discuss four case studies. We first review the recent progress in the characterization of the structural and mechanical properties of wood at multiple scales. We then review and discuss the universal concept of cooperativity in biological materials that governs how they are synergistically integrated at multiple scales. We also provide an example of the use of carbon nanotubes as a building block to form bio-inspired yarns with superior mechanical properties that rely on the concept of



**Figure 2.** Illustration of the general design process of bio-inspired materials. This process starts by investigation of a biological material with outstanding material property and follows by applying the learnt principles to build a physical model and using category methods to extract the most relevant parameters that yield the material property of interest, systematically optimizing the design by adjusting these parameters and using the knowledge to make and test specimens. These critical steps form a complete loop of rational material design.

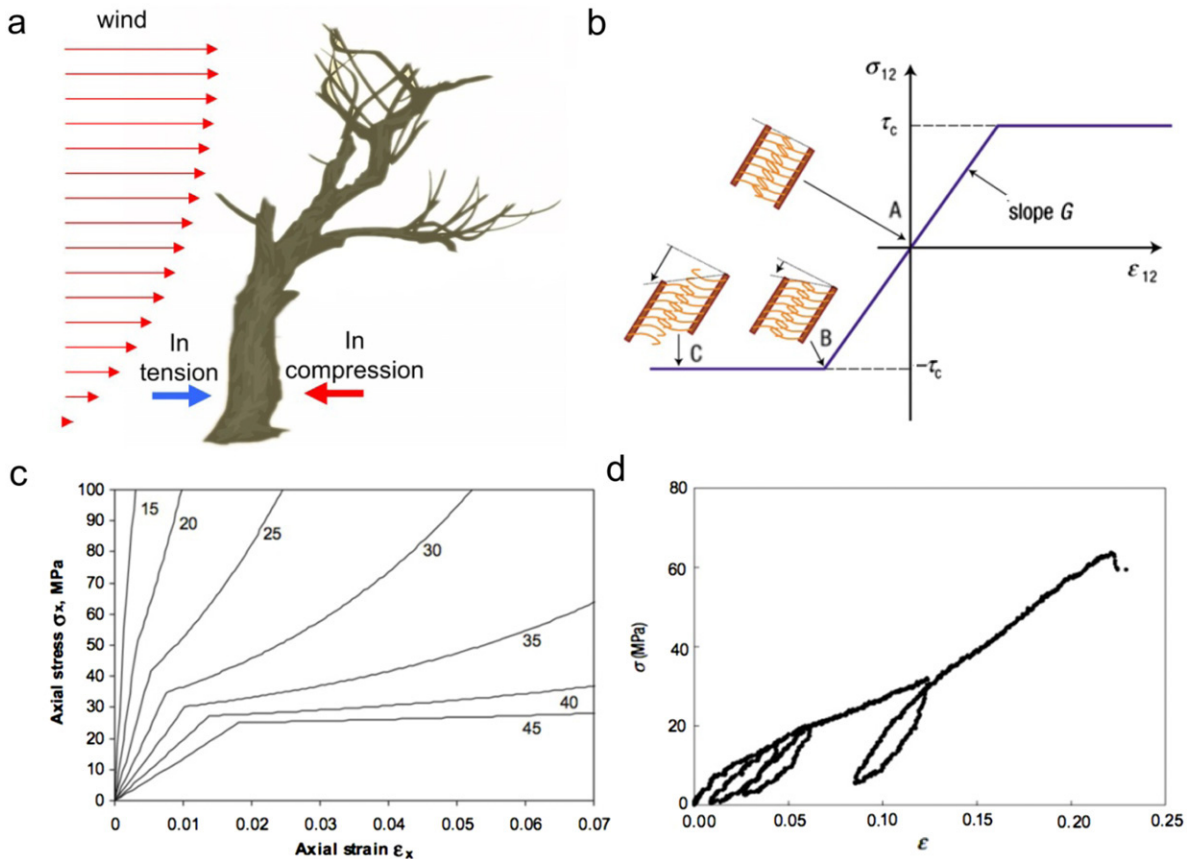
cooperativity. Last, we introduce an additive manufacturing technique to facilitate the rapid realization of hierarchical material structures from the micrometer scale upwards, for mechanical tests. These case studies demonstrate the use of physical insights in the bottom-up and rational design of materials, and they show the breadth of approaches that can be exploited towards progress in this field.

## 2. Case study I: structure and mechanics of wood

Wood is a fascinating example of the complexity and capabilities of natural materials. With little variation in chemical composition, many species of plant life grow this material, varying its mechanical properties to resist the massive forces and moments of weight and wind with remarkable efficiency, as illustrated in figure 3(a). Naturally, as it is the product of multicellular life, wood is a cellular material. The advantages of a cellular structure are manifold [9]; a cellular solid is less dense than the solid wall material, and by adjusting the thickness of the walls, and the shape and orientation of the cells, the density, elasticity, failure modes, and even anisotropy can be precisely tuned and controlled [10, 11]. In trees, long tubular cells are oriented parallel to the trunk or limb [10], allowing any axial stress to be taken by tension or compression of the cell wall material rather than bending of the cell walls—though for other load conditions, such as horizontal impacts, the bending of the cell walls is helpful in dissipating energy [10, 12].

Ultimately, all of the potential properties of cellular solids scale (depending on geometry) with the properties of the

solid material of the cell walls [9], and it is here that wood excels. Fundamentally, the cell wall material is composed of sugar, but it is the arrangement of these polysaccharides that makes all the difference. Long fibrils of crystalline cellulose are oriented parallel to one another, embedded in a matrix of amorphous hemicellulose, stiffened by lignin [13, 14]; this composition is the root of two important qualities of wood: the ability to deform plastically, and the ability to modulate the axial stiffness [14–18]. The stiff fibrils in the pliant matrix are similar in functionality to steel rods reinforcing concrete [14, 19–21]: the strongest qualities of each of the constituents compensate for the weakest of the other. The crystalline fibrils are incredibly stiff, with a modulus near 200 GPa [22–24]. Such rigidity, however, comes hand in hand with inextensibility. The flexible matrix that glues these fibrils together ends up reducing the modulus from that high value, and allows the material to stretch and fail through the weaker phase, dissipating more energy at a slower rate than it would through fracturing the crystalline phase [25, 26] (this feature is also found throughout nature, such as in bone or nacre) [9, 27–29]. When steel-reinforced concrete fails, and the steel is stretched further than the concrete can keep its hold and they debond, that failure is total and final. When the cell wall material is stretched beyond the point at which the matrix can maintain its static hold on the fibrils, what is known as the stick–slip mechanism comes into play. All of the fibril–matrix bonding is done via hydrogen bonds [17, 30], and when these bonds are broken, neither the fibril nor the matrix sustains any damage [31], and the bonds simply reform at another location along the fibril, relaxing the stress of the extra strain [15].



**Figure 3.** Deformation of tree and wood under loading. (a) A schematic of a tree deformed by wind, leading to one side in tension and the other side in compression. (b) A schematic of the theoretical model that explains the elastic–plasticity of wood under loading. Elastic shear occurs from the undeformed state A until point B with the shear modulus  $G$ . At point B, the critical shear stress is reached, and further deformation occurs at constant stress by an irreversible gliding of the matrix. Reprinted from [31]. (c) Stress–strain curve for the low-strain behavior for varying microfibril angles (MFAs), highlighting the MFA–stiffness relationship. Reprinted from [17], copyright 2008, with permission from Elsevier Bottom. (d) Stress–strain response of a single tracheid undergoing four loading cycles. After each unloading the initial stiffness is recovered before the cell yields again, and, at high strain, the yielded stiffness increases greatly up to fracture. Reprinted from [31], copyright 2003, with permission from Nature Publishing Group.

This results in a two-phase stress–strain behavior: with a high initial stiffness while the hydrogen bonds are all intact and contributing, and then with a lower stiffness as they break and reform continually, while the fibrils glide through the matrix, as shown in figure 3(b).

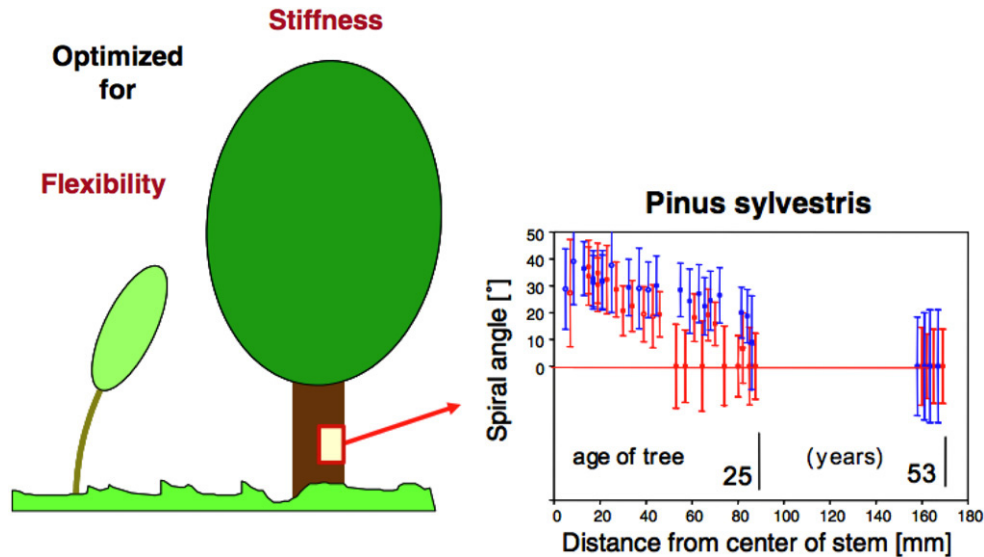
Much as the orientation of cells controls the anisotropy of the bulk, the orientation of the cellulose fibrils controls the anisotropy of the cell wall material. Under strain that is normal to the direction of the fibrils, the direct compression or extension of the matrix results in a lower Young’s modulus than for strain parallel to the fibrils, which invokes their superior modulus while shearing the matrix. The modulus in between these two orientations varies between the extremes [32]. By modulating the orientation of the fibrils within the cell, the axial stiffness can be controlled without varying the cell wall thickness [10, 16, 17, 33, 34] (as opposed to increasing the modulus by increasing the relative density via thicker walls).

In the thickest layer of the wood cell wall (and thus, the layer most directly contributing to the axial properties) [14], fibrils are arranged helically about the cell axis. The pitch of the helix measured relative to the axis is known as the microfibril angle (MFA). When the MFA is relatively large

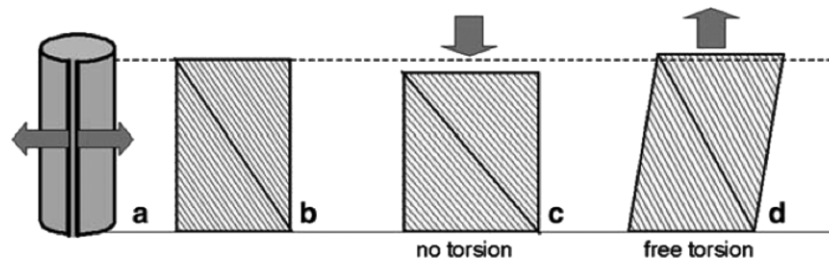
( $45^{\circ}$ – $50^{\circ}$ ), the cell deforms by twisting and elongating as the helix unwinds [33]. The continuity of the material as this unwinding takes place is due to the aforementioned stick–slip mechanism, allowing the strain to unwinding to continue until the fibril orientation approaches being parallel. Since the MFA continues to modulate the axial stiffness after the static hydrogen bonds have yielded and fibrils are gliding through the matrix, the gradual reorientation of the fibrils adds a third phase to the two-phase stress–strain behavior of the wall material alone: a large-strain stiffening before fracture. Figure 3(c) details the dependency of the stiffness on the MFA in all three phases of deformation based on analytic models [17, 31], and figure 3(d) plots the three-phase deformation behavior of an actual cell, showing also the recovery of pre-yielding stiffness upon relaxation and reloading.

The ability to modulate the stiffness independent of density is interesting enough from a purely materials standpoint, yet to the living growing tree it is crucial to structural stability, and thus to survival. A young tree will build a flexible trunk to handle high winds by bending and minimizing its exposed area, whereas an older tree with a thicker trunk (to support the larger crown weight) cannot bend and must resist. Measuring





**Figure 4.** Microfibril angle variation from pith to bark, highlighting the flexibility of the young tree (in blue) and the stiffness of the adult tree (in red). Reprinted from [10], copyright 2007, with permission from Elsevier.



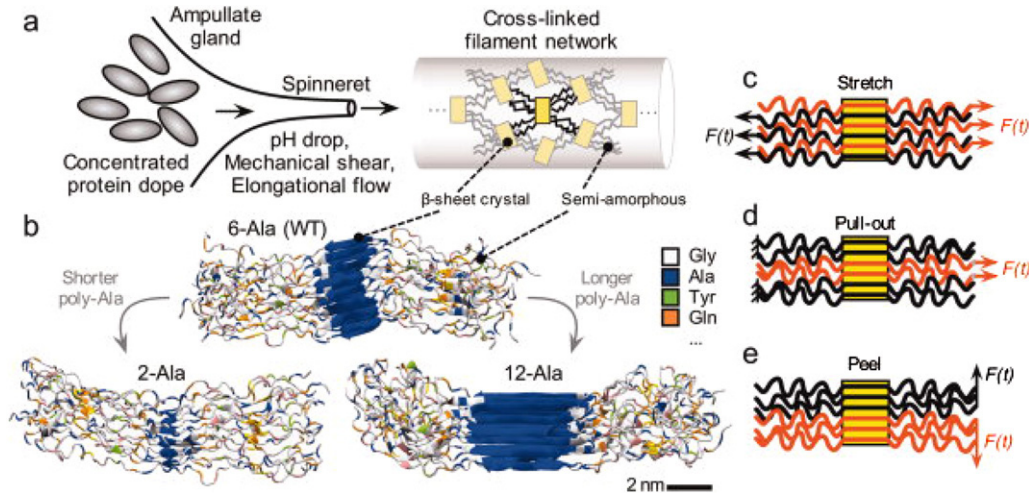
**Figure 5.** Schematic of an inextensible fibril model for a cell wall. When the total area is increased due to swelling, preventing torsion causes the cell to contract, while allowing it causes the cell to extend, respectively inducing internal tension or compression. The black line is of constant length, representing the inextensibility of the fibrils in this model. Reprinted from [35], copyright 2007, with permission from Springer.

the MFA at different radial distances from the pith reveals the first part of this vertical stability strategy: near the pith, the wood, that is in essence of the young tree's trunk, is flexible with a high MFA, while the wood closer to the bark is much stiffer, with nearly zero MFA, which, with its larger circular area, makes it incredibly rigid in bending [10, 35, 36]. Figure 4 plots these MFA measurements and shows a schematic of these different wind-resisting strategies for young and old trees.

The second and maybe more crucial part of this vertical stability strategy lies in the tree's ability to generate internal stresses [37, 38]. As previously mentioned, the molecules that make up the cell wall interact primarily via hydrogen bonding, and this makes the walls very responsive to moisture content. Depending on the MFA and the boundary conditions of the cell (longitudinal or torsional constraints), different magnitudes and directions of internal stress can be generated. Figure 5 shows a simplified schematic of how a cell constrained in torsion can shorten, inducing tension, while the same cell, unconstrained in torsion, will elongate, which means that, given the axial constraint due to the arrangement of the cells within the tree, the elongations or shortenings become induced

internal compression or tension, respectively. In the case of the adult tree trunk, the high-MFA cells near the bark are rectangular in cross-section, and their close packing prevents them from twisting, while the cells near the pith are rounder, with weaker interconnections. Thus the center of the trunk generates compression while the outer rim generates tension, which serves to actively increase the bending rigidity of the trunk as well as guarding it against buckling [35, 37, 38]. This mechanism is very similar to the outrigger mechanism for tall buildings: the main building core takes all of the compression, and around the edge, closer to the façade, tensioned members tie down into the ground, effectively acting as a rotation spring to supplement the passive bending rigidity [39].

This technique of controlling the stiffness and internal stresses allows a tree trunk (or almost any plant stem, for that matter) to reorient: a tree growing diagonally out of a sloped surface will apply tension to the topside and compression to the bottom to reorient closer to vertical [37]. An example of how precise and efficient a living tree is at controlling these factors can be found in branches. A branch, cantilevering out of the tree trunk, will grow stiff tension cells at the top and



**Figure 6.** Fiber formation and loading modes of spider silk proteins. (a) A combination of chemistry and shear flow transforms the concentrated protein dope into a network cross-linked by aligned crystalline overlaps held by aligned hydrogen bonds. (b) Predicted crystalline regions and surrounding extensible strands for cases wildtype and mutated protein sequences. Many loading modes are predicted among the crystalline regions, including (c) stretching of alternative strands, (d) the pull-out of central strands, and (e) peeling. Reprinted from [75]. Copyright 2001, with permission from Wiley Periodicals, Inc.

soft compression cells on the bottom to resist the increasing moment due to its growing length and thickness while keeping its orientation [10, 40]. Not only will it resist the new loads and keep its orientation, but it will do it nearly perfectly, controlling the gradient of stiffness and stress through its cross-section such that the strain at the connection to the trunk is distributed nearly perfectly uniformly [12]; the branch will only fall if it snaps along its length, or if a section of trunk pulls out with it because the connection is a point of strength rather than a weak link.

Nature has had a long history of developing this efficient and adaptable structural material. As such, wood is essentially perfectly designed for its functions. For a much shorter time, mankind has been taking advantage of this product of nature, using tree trunks as columns and foundation piles with inherent vertical stability or cuts of trunk for flexural members for floors and roofs of stone structures. However perfect a material wood is in nature, it can never be perfect for our synthetic applications. What we can do, though, is draw inspiration from it; we can design and create our own materials, precisely tuning the properties, and controlling the stresses the way the tree does, but without the irregularities and nonstructural elements of natural grown wood, such as material transport channels or knots from branches, that come about from its source in a living, growing entity.

### 3. Case study II: cooperativity in protein molecular structures as a universal paradigm to turn weakness into strength

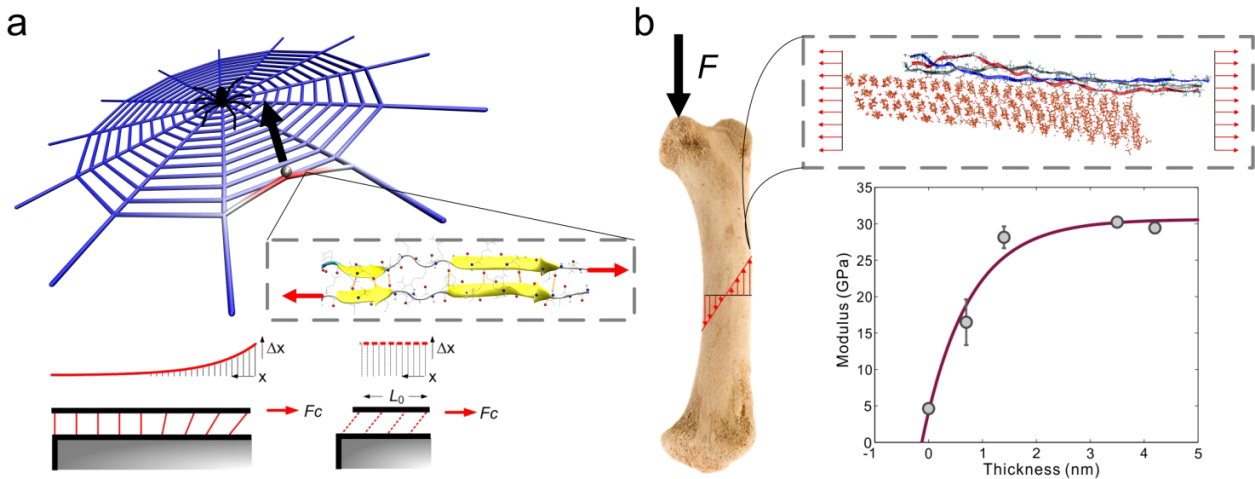
The molecular structure of protein materials, which defines how amino acids are linked into chains, fold, entangle, and assemble with each other, determines its material property. The evolution of nanotechnology provides tools that enable us to quantitatively measure these effects and include these factors

into the design of the chemical composition and structure of novel materials. This contributes to our ability in the rational design of biological materials, providing more degrees of freedom and making it possible to use universal building blocks to achieve diverse functions in spite of weak building blocks [7].

Many protein materials have been studied closely in recent years, and their material properties have been revealed both in experiments and *in silico* [2]. It is found that they have material properties exceeding those of most engineering materials, suggesting the importance of molecular structure. Among such materials, spider silk presents a prime example of a natural fiber that combines strength and toughness to make a thin fiber with exceptional energy absorption capacity that can catch flying insects or birds and return to its original length [41, 42]. Through spectroscopy and molecular dynamics simulations, it has been found that spider silk proteins within the fiber form a network of extensible amorphous strands that interconnect via strong beta-sheet crystals that resist shear failure through the cooperativity of aligned hydrogen bonds [43–45], as shown in figure 6. While the combined strengths of the relatively weak noncovalent hydrogen bonds can resist shear failure, they can also reform after the protein strands have been torn apart after catching large prey. It is identified that the displacement along the backbone of silk peptide is as an exponential decay function of the coordinate as [6, 8]

$$\bar{\Delta} = \exp(-x\sqrt{K_2/K_1}/b), \quad (1)$$

where  $\bar{\Delta}$  is the local displacement normalized by the maximum displacement at the point under loading,  $x$  is the coordinate of the local point as  $x = 0$  is the point under loading,  $b$  is the distance of two neighboring hydrogen bonds,  $K_1$  is the stiffness of the backbone chain, and  $K_2$  is the stiffness of the hydrogen bond that connects different backbone chains.



**Figure 7.** Nanoscopic mechanism of spider silk and bone in deformation. (a) Deformation in spider web causes the stress applied to beta-sheet structures in silk. It is identified that 3–4 neighboring hydrogen bonds work in a cooperative way that yields the same strength as many more hydrogen bonds. Reprinted from [6]. (b) External force applied to bone causes its basic building block, the combination of tropocollagen and hydroxyapatite, subject to stress. Here it is shown that the hydroxyapatite in nanometer thickness is crucial for the tensile modulus of the combination. Reprinted from [55]. Copyright 2012, with permission from the American Chemical Society.

From equation (1), the characteristic length defined as the cooperatively length constant is

$$L_0 = b\sqrt{K_1/K_2}. \quad (2)$$

It is noted that here  $L_0/b = \int_0^\infty \bar{\Delta} dx/b$ , which means that, for interactions that can be modeled by linear springs (which is the case for hydrogen bond and backbone in silk), the strength exerted by interfacial materials of length  $L_0$  equals that of the much longer structure, as shown in figure 7(a).

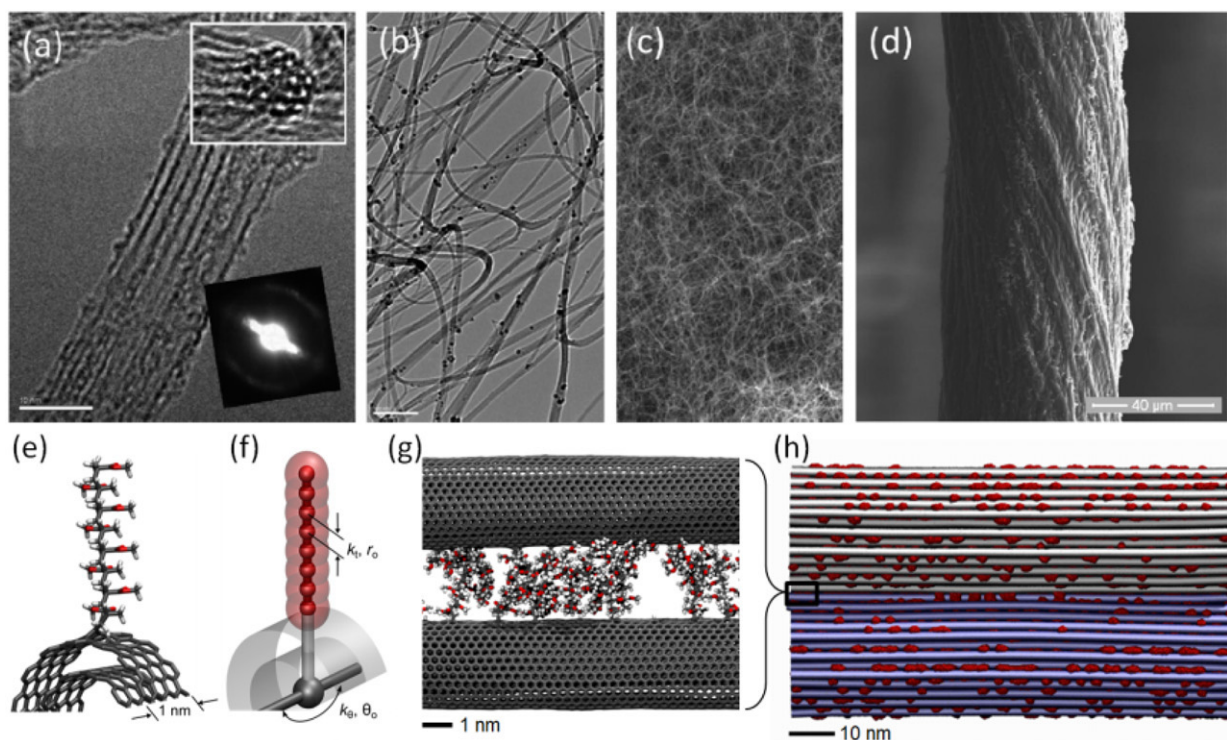
This characteristic is not unique in spider silk but generally exists in many biological materials and affects their stability and mechanics [6] (also see figure 7). Amyloids are primarily composed of beta-sheet structure of strong cooperativity for the hydrogen bonds between neighboring chains, and thus it is not surprising to find that they can form long fibril structures both *in vivo* and *in vitro* [7]. Hydrogen bonds in alpha-helix structures are generally of less cooperativity, and they yield short helical domains [46]. This is supported by the evidence that there are no single long alpha helices found in nature, but that they are almost exclusively found in the forms of coiled coils, triple helices, and even higher-order helical structures. It has been found experimentally that protein materials rich in alpha-helix content (such as wool, hair, hoof, and cellular proteins) under mechanical deformation have intrinsic intention to change their secondary structure into a beta-sheet structure [47]. By studying the unfolding and refolding process of alpha-helical structures, it is revealed that the occurrence of the transition is governed by the competing of the strength between alpha-helix and beta-sheet structures, which relates to the comparison of the cooperativity between the two structures. The protein structure after transition has a significant increase in the stiffness, strength, and energy dissipation capacity at large deformation (figure 7(a)).

By quantitatively investigating the relation between the structure and function of protein materials, we learned that

the distribution and property of weak interactions, such as van der Waals forces, hydrogen bonds, and electrostatic interactions, need to be combined with the property of the strong interactions to reach great strength [6]. Water is a material with a very simple molecular structure, yet it is important for life, and enables many key biological functions. It forms ice crystals of high strength at low temperature as the water molecules organize in an ordered way (and are interconnected by a regular network of hydrogen bonds). This architecture is crucial for ice's stability. Studies of the fracture and melting of ice reveal that even single point defects can lead to its failure, the hallmark of a brittle material [48, 49]. In contrast, bone and many bone-like composite materials have a well-known toughness that is able to be subjected to high loading and impact despite the existence of defects [50–52]. It is now understood that the defect tolerance of these materials is caused by their material composition and microscopic architecture. For example, bone is constructed from two primary material phases that feature distinctly different mechanical properties, namely collagen and hydroxyapatite, which form building blocks of nanometer size and are staggered to combine with each other in a hierarchical pattern [53–55], as shown in figure 7(b). This intricate structure of bone from the molecular scale up contributes greatly to the material's toughness, as it is able to dissipate the deformation energy as well as elongate the failure pathway.

As these examples showcase, natural materials provide a very rich database of biological materials. Many of them have fascinating mechanical and biological functions at very low energy consumption, and with simple basic material building blocks. By systematically investigating the mechanisms and performing a comparative analysis, we can reveal the fundamental physics of these materials and design new engineering materials with improved material properties and with lower production energy cost. Moreover, such analysis can also





**Figure 8.** Hierarchy of double-walled nanotube (DWNT) materials. (a) Individual DWNT bundle. Scale bar: 10 nm. (b) TEM image of interconnected DWNT bundles including Fe particles. Scale bar: 100 nm. (c) SEM image of a DWNT mat. (d) SEM image of a DWNT yarn. (e) Atomistic and (g) coarse-grain models used for molecular dynamics simulations showing DWNT cross-section and covalently attached polymer. (f) Atomistic model showing polymer adhesion between two DWNTs at the (h) interface between two coated bundles. Computational modeling was used to explore the effects of polymer length and density. Adapted from [63]. Copyright 2012, with permission from John Wiley and Sons.

contribute to digital additive manufacturing that generates the product in a more controlled and direct way [56]. We now proceed with two examples of how such realizations can be achieved in completely synthetic materials.

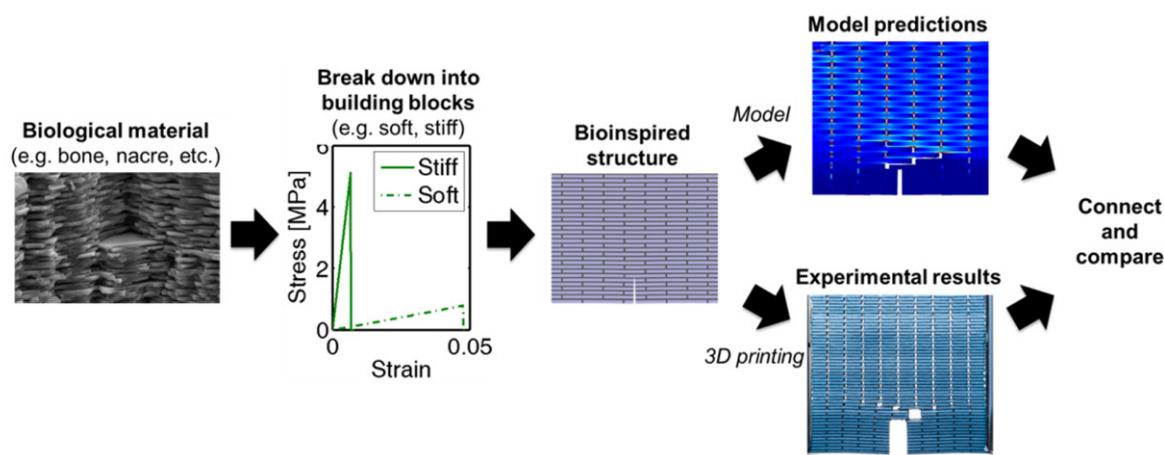
#### 4. Case study III: bio-inspired CNT-based fiber design

Twisted, braided, and woven fibers have been used for thousands of years for fastening, tensile loading, and energy absorption in armor. These general applications remain consistent, but the available materials can now be designed for a specific application and environment, and for other engineering factors. Natural cellulose- and collagen-based fibers have been replaced in many areas with synthetic polymers, para-aramids, and carbon-based materials, but the mechanisms by which the fibers fail still present design challenges.

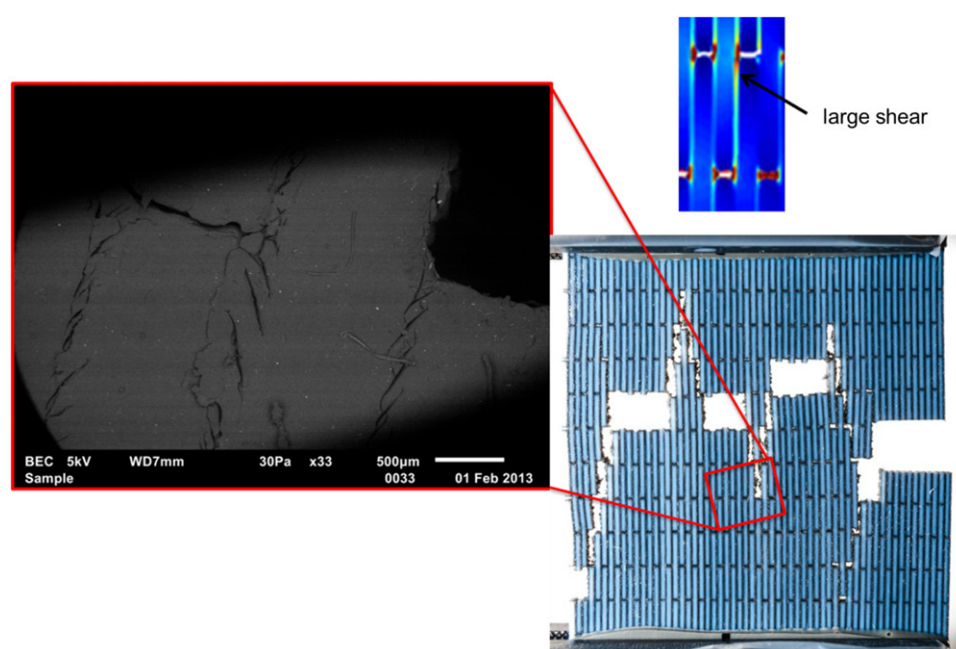
Conventional yarns are twisted and spun from individual strands that do not span the entire length of the yarn, so failure is an interplay between the tensile strength of the strands and the shear load transfer among the strands. Carbon nanotubes (CNTs) are found to be extremely stiff and strong, and they have been used in nanocomposites to improve their mechanical and thermal properties. It is quite crucial to study how to braid CNTs into yarn because individual CNTs cannot be grown to relevant scales of meters and beyond. This necessitates a need to connect distinct CNTs such that mechanically strong

interfaces are created. However, CNTs have poor shear load transfer across their atomically smooth surfaces [57]. Covalent carbon bridges have been investigated in order to increase the connectivity, but noncovalent hydrogen bonds present the distinct advantage of reforming after large deformations within the CNT network. Inspired by protein materials like spider silks, functionalized CNTs are used to fabricate yarns, which are integrated by weak interactions but are expected to still have comparable strength to that of pristine CNTs. For example, the carboxyl group as a functional group has the ability to form two hydrogen bonds between two pairing carboxyl groups [58]. A variety of other functional groups (e.g., OH, NH<sub>n</sub>, CH<sub>n</sub>) can be explored to engineer the bonding between functionalized CNTs [59–61]. It is also found that the grouping of functional groups into clusters along the CNT axis has potential strategies to improve the cooperativity of deformation and thus can more efficiently bond CNTs [58].

Mixing polymer chains with CNTs can form arrays of hydrogen bonds as sacrificial sites for gradual failure, leading to a useful design tool in synthetic fibers inspired by spider silk, tendon, and other energy-absorbing natural fibers. However, without bonding between the polymer and the CNTs [62], pristine CNTs lack sufficient adhesion force for polymer attachment. Recent experimental work aided by molecular dynamics simulations has yielded a fiber made from double-wall CNT bundles formed in a CVD reactor and functionalized by being covalently coated with ultra-short



**Figure 9.** Schematic of a design process for the design of functional biomimetic composites. Key structural features of biological materials are abstracted and translated to a computational environment. The design is driven by structural optimization as governed by the tension–shear model. Finally, the computational model is translated to a tangible structure by additive manufacturing, and fracture mechanisms as well as mechanical properties are compared and connected.

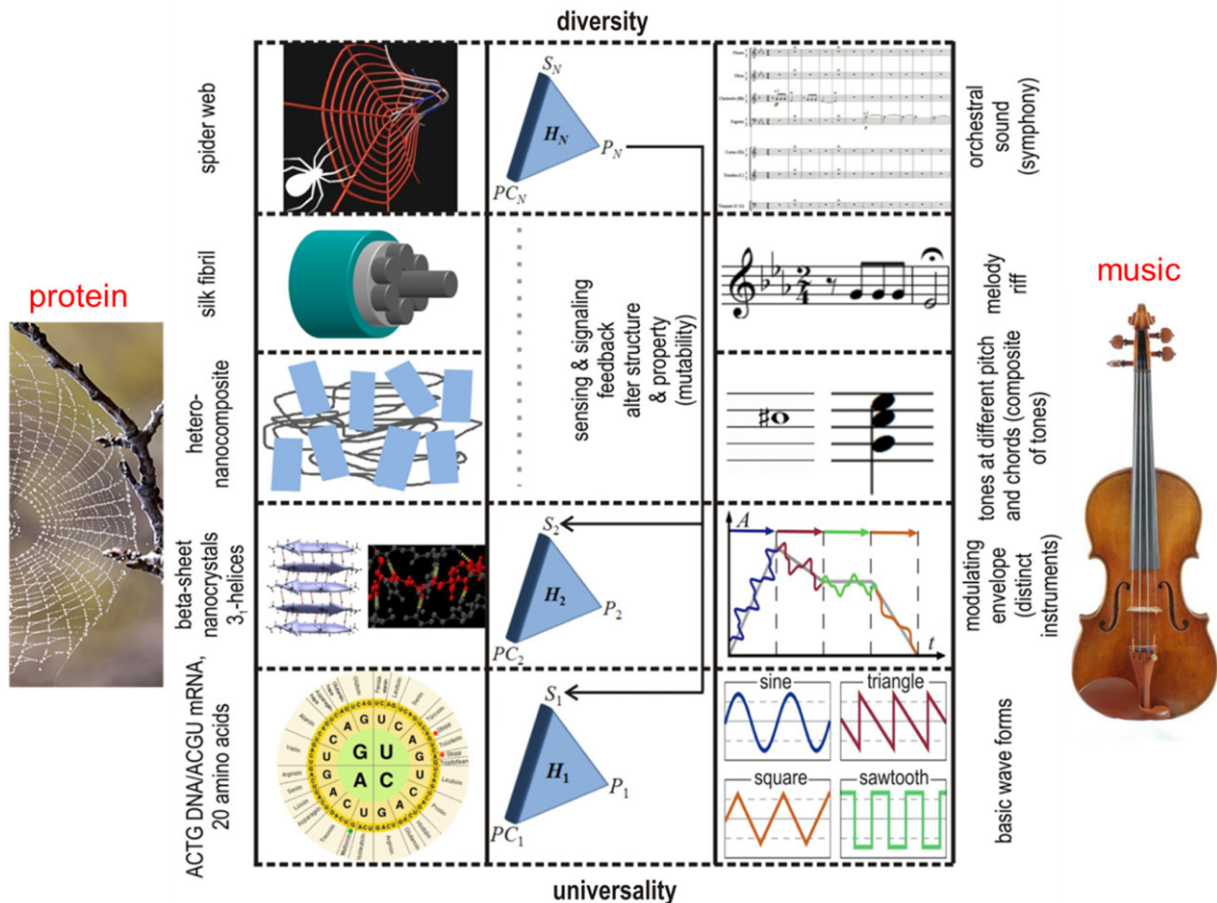


**Figure 10.** Schematic showing final fracture pattern through the bone-like topology along with close-ups of the combined tension–shear matrix failure for experimental and computational specimens. For illustrative purposes a section of the tension–strain field plot is shown for the computational specimen. The schematic clearly displays the dominant tension–shear damage mechanism driving the superior fracture resistance of the bone-like specimen. The shear damage is visualized by the periodically occurring inclined fractures along the long edge of the platelets. The tension damage is visualized by the connected fracture along the short edge of the platelets.

polymers with microstructural similarities to spider silk [63], as shown in figure 8. Since the polymers are covalently bonded to the CNT sidewalls, and each polymer presents many hydrogen bonding sites and van der Waals interactions, shear load transfer between overlapping bundles becomes very effective. With overlap lengths observed experimentally, the combined strengths of the hydrogen bonds can be so large that the CNTs on the bundle surface fail in tension before the bundles shear apart. Being intertwined, the yarn network can extend by aligning the bundles along the tensile direction until the overlap sites get loaded directly in shear, much like

the deformation of extensible protein chains and crystalline overlaps in spider silk.

As more synthetic materials are presented for next-generation fiber production, their chemistries and composite nanostructures can be greatly aided by mimicking natural materials. However, there still remain hurdles in translating mechanisms between natural and synthetic materials as well as overcoming size effects. Computational design methods such as molecular dynamics simulations can now be used to predict effective chemistries and model nanostructures to aid experimental synthesis in deciding on design factors. In this



**Figure 11.** The universality and diversity of biological materials and its analogical comparison to music. The tens of thousands of protein structures in the protein data bank are all composed of a few basic amino acids. They differ in how the amino acids are arranged and how they interact with each other. The existence of a hierarchical arrangement of these amino acids makes the number of possible structures become infinite, and arrangements at different hierarchies are synergistically incorporated to yield the exceptional performance of the material. This principle is similar to what are known in music and other arts, as well as linguistics, since the basic building blocks in these art forms should have well designed structures to achieve certain functions [64].

way, the computational model can act as a bridge between the reverse-engineering studies of natural materials and the direct design of synthetic fibers.

#### 5. Case study IV: 3D printing—rapid manufacturing of bio-inspired materials from the bottom up

Recently, 3D printing has been used as a technique to rapidly manufacture a range of functional materials [65–70]. Additive manufacturing presents a very exciting outlook for the synthetic design of biomimetic materials as the most recent technology allows a precise control of structural design at fine length scales. Moreover, the most advanced printers can print a multitude of materials with widely contrasting constitutive behavior simultaneously in one structure to create advanced composites from micrometer scales upwards. A recent study in our group explored a novel design process for biomimetic materials [56]. The process is illustrated schematically in figure 9. In this process, multiscale modeling techniques and computational structure optimization were combined with additive manufacturing to create composites

with fracture characteristics far superior to those of their stronger constituents. Printed composites with bone-like (brick-and-mortar) topology exhibited fracture resistances more than 20 times larger than that of their strongest constituents [56].

A fundamental goal of the approach was to create structures replicating some of the notable fracture mechanisms observed in both bone and nacre. Specifically, the earlier work [56] sought to isolate the deformation mechanisms associated with the topological arrangement of stiffer and softer constituents in the respective biomaterials. Figure 10 displays a characteristic fracture pattern through the bone-like topology along with a microscopy image and a corresponding snapshot of the longitudinal strain field retrieved from simulation. The overview image of the entire fractured specimen shows an intriguing step-like fracture propagating through large portions of the specimen. The microscopy and snapshot from simulation give insights to the mechanisms controlling the propagation. A key mechanism is the cooperative action of shear in the soft phase along the long end of the platelets and tensile strain in the soft phase along the short end of the specimens. The large tensile strains are expressed through the periodic



separation along the short edges of the platelets throughout the entire specimen. Correspondingly, the shear damage presents itself in the microscopy image as the periodically occurring inclined fracture lines. Analysis by Gao *et al* has shown that biological composites such as nacre and bone in fact tune the aspect ratio of the stiffer plates to optimize the cooperation between shear and tensile damage [71].

The initial models developed managed to correctly predict the main damage mechanisms and qualitative trends in mechanical behavior of the printed composites. As this first effort demonstrated the viability of this novel design process, further efforts should focus on refining the design loop to improve the predictions and attain quantitative predictability.

## 6. Discussion and outlook

The design of biologically inspired materials with predictive properties requires tremendous care. The variation in its basic unit and the formation of hierarchical arrangements render 'infinite' possibilities. However, one may design and improve biological materials according to the existing nature database. For example, there are tens of thousands of naturally occurring protein structures available in the protein data bank. Their atomistic coordinates and secondary structures are available, but their mechanical (and other material) functions are not well documented. Computational simulations provide tools to investigate their material properties and increase our knowledge of how the protein mechanics relates to its sequence [3]. We need to combine computational models with experimental tests and statistics methods such as bioinformatics to gain a precise and comprehensive understanding of material behaviors at multiple scales (figure 11).

Biological materials have many fascinating advantages that cannot be reached by merely using engineering materials. Successful design and fabrication of these materials will have a giant impact on manufacturing and scientific fields. For example, their biocompatibility and robustness make them ideal materials for biomedical applications, such as implants for plastic surgeries, artificial arteries, matrix material for neural repair, or carriers of embedded electronics in the human body [72, 73]. In addition, the self-healing characteristics of some biological materials would contribute to increasing the material's lifespan, enabling materials to recover from a state with buckling or small cracks to a normal status in a suitable environment. Moreover, based on their tunable mechanical properties, biological materials may have the potential to be used with the purpose of energy harvesting. They absorb chemical energy in environments and turn it into kinetic energy [74].

Understanding the fundamental mechanism of how a biological material works is critical for manufacturing its counterparts. The produced materials can have similar material functions as the natural ones, but may use different raw materials like polymers to achieve them. An example is our recent work on the design and fabrication of nacre-like structures (see section 5) [56]. These material designs are extracted from a rich database of mineralized biomaterials, designed, analyzed, made, and tested, and results have demonstrated that composite

synthesis using additive manufacturing is a possible route for innovation. Such advances are important for manufacturing, architecture, bioengineering, space exploration, and many related areas, and they allow a material design and synthesis process from the micrometer scale upwards.

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