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Scripta Materialia 68 (2013) 8–12
Scripta MATERIALIA
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Viewpoint Paper

Multilevel architectures in natural materials

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Available online 5 June 2012

Abstract—Nature's materials are structured at multiple length-scales, allowing organisms to adapt to external stimuli for given (even multiple) functions. Hierarchical structuring, which is a simple consequence of (adaptive) growth, is illustrated by four examples from nature: wood, bone, the skeleton of a glass sponge and lobster cuticle. All of these use material architecture to combine simple building blocks into complex functional structures. In addition to helping understand biological function, such systems are studied to inspire development of novel synthetic materials.

Keywords: Biomaterials; Composites; Bone; Porous material; Architectured materials

1. Introduction

From the point of view of an engineer, there is a surprisingly small selection of component materials in nature's toolbox. They comprise a handful of minerals (e.g. calcium carbonate, calcium phosphate, silica), and a range of polymers, based either on protein (e.g. collagen, silk) or on sugar (cellulose, chitin) [1]. Despite this, nature produces a wide variety of materials or structures with a remarkable range of material properties [2]. This is achieved by combining these simple components into natural composites [3] with a maximum of control over shape and structure on many length scales [4]. This hierarchical structuring allows materials to be grown in a self-organized manner, but also allows the structure to be adapted to needs at each of the different scales. A better understanding of how nature controls material architecture at multiple levels and, in turn, the role structure has on function may lead to new design concepts for bio-inspired materials [1]. This paper gives a short overview of multi-level architectures found in natural materials and their role on function, and illustrates this with the examples of wood, bone, deep-sea sponge skeleton and lobster cuticle. For more detailed overviews of the design of biological materials, see Refs. [4–6] and the citations contained therein.

2. Wood

Depending on the length scale, wood can be viewed as a fibre composite, a honeycomb or a functionally graded material (Fig. 1). This structuring is achieved through the combination of only a few constituent materials – stiff crystalline cellulose nanofibrils, embedded in a softer hygroscopic matrix of a few other polysaccharides and lignin (Fig. 1a). Due to the high relative stiffness of the cellulose fibrils, this leads to significant anisotropy in the material properties. By simply controlling the microfibril angle, μ, at which these fibrils are wrapped around the lumen of the wood cell (Fig. 1b and c), it is possible for the tree to vary the mechanical properties, from high stiffness at small angles to more flexibility at larger angles [7]. This enables the growing tree to start out with a highly flexible stem which is gradually stiffened when the height to thickness ratio decreases during maturation [8]. Wood cells in turn make up a honeycomb-like structure (Fig. 1d and e) that is stiff and lightweight, and can transport fluids through the lumen of the cells themselves. The consequence is that wood exceeds most engineering materials in the figure of merit for building high columns with the lowest amount of material (that is, E/ρ^2, where E is Young's modulus and ρ is the density [4,9]. The shape of the cells is thought to control the torsional constraints on the cell, which in turn help control the resultant tissue stiffness [10]. Finally, at larger length scales, the tree can produce gradients in architecture [11], as schematically shown in a spruce branch in Fig. 1f). During growth, the tree responds to the mechanical loads experienced

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1359-6462/$ - see front matter
http://dx.doi.org/10.1016/j.scriptamat.2012.05.045

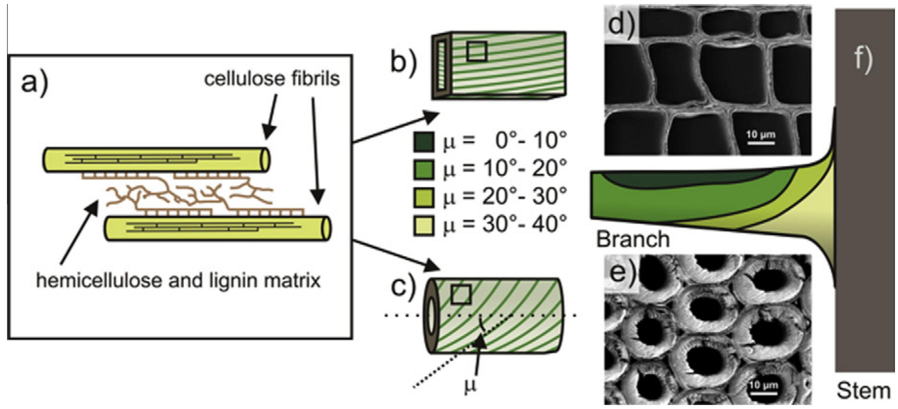

Figure 1. Wood is architectured at many different length scales. (a) The cell wall consists of stiff crystalline cellulose fibrils embedded in a softer matrix of hemicelluloses, pectins and lignin. (b) Schematic of a single opposite wood cell spirally reinforced with cellulose fibrils at a low microfibril angle. (c) A single round compression wood cell reinforced with high microfibril angle cellulose. The dotted line defines the microfibril angle, μ. (d) Scanning electron micrograph of opposite wood showing the square honeycomb structure. (e) Scanning electron micrograph of the honeycomb of round compression wood cells. (f) The distribution of cellulose microfibril angles, μ, in the tissue of a spruce branch. Part (a) was based on Ref. [7]; (b) and (c) were based on Ref. [10]; (d) and (e) were kindly prepared by M. Eder; and (f) was based on data in Ref. [11].

in the tissues by producing stiffer tissues on the upper side of the branch and more flexible tissues on the lower side. Due to the high microfibril angles present in the compression wood on the lower side of the branch, a swelling of the hemicellulose matrix will lead to cell extension and high compressive stresses, thus helping to support the weight of the branch as the tree grows.

3. Bone

Bone is a hierarchical material [12] consisting of collagen, hydroxyapatite, some non-collagenous proteins and water. The main constituents of bone alone are either too flexible or too brittle to be used as reliable structural materials (Fig. 2a). However, their astute combination can produce a material that is both tough and stiff [2]. The reinforcing mineral particles in bone are nanoscaled (Fig. 2b), which means they are too small to contain critical sized defects, thus enabling them to operate close to their theoretical strength [13]. The bundles of the mineralized collagen fibrils are then "glued" together by non-collagenous proteins to make up micron-sized fibre bundles (Fig. 2c and d). This "glue" is thought to be responsible for the plasticity observed in bone [14] and to help dissipate energy during fracture [15], partly explaining the high toughness of bone [16]. The lamellar structure of bone seen at larger length scales (Fig. 2e) affects not only the anisotropy of bone stiffness and strength [17], but also the resultant toughness, which is strongly orientation dependent [18]. Such lamellar structures can be found in osteons, for example (Fig. 2f), wrapped around channels containing blood vessels within compact bone. Such blood vessels are needed to irrigate the cells that are spread throughout the bone matrix (Fig. 2g). These cells are needed because bone is not just a structural material, but is also an organ that serves as ion reservoir, keeping calcium and phosphate levels in the body within their physiological ranges [19]. As a consequence, bone is riddled with a complex network of cells (Fig. 2h), called osteocytes, which are thought to be responsible for the mechanosensitivity of bone through their ability to communicate with each other via the interconnected canaliculi [20].

4. Glass sponge

The skeleton of the deep-sea sponge, *Euplectella* sp. (Fig. 3), consists almost entirely of silica, with a small amount of protein [21,22]. At macroscopic length scales (Fig. 3a) the skeleton of the sponge is made up of a square lattice of silica struts cross-braced with diagonal elements (Fig. 3b), something rarely seen in nature. These struts can be viewed as having a ceramic fibre-composite structure consisting of multiple spicules joined together in a silica matrix (Fig. 3d and f). These struts connect to each other via joints reinforced by laminated layers of silica (Fig. 3c–f). Laminated structures can also been seen in the spicules themselves (Fig. 3g), and consist of relatively thick layers of silica glued by a softer layer of protein (Fig. 3h). Like with the lamellar structure found in bone (see above) and nacre [23,24], this laminated structure plays an important role in hindering crack propagation [25], an observation which has led to new concepts for strong laminates [26]. Finally, nanoparticles of silica are the building blocks of each silica layer at the smallest length scale (Fig. 3i). The glass spicules with build the skeleton are remarkable not only for their mechanical but also for their optical properties, being able to transmit light in a similar way to man-made optical fibres, despite being formed themselves at ambient temperatures [27].

5. Lobster shell

Arthropod cuticles, such as those found in the lobster *Homarus americanus* (Fig. 4, from Ref [28]), are built of a chitin–protein fibre composite material [29] reinforced by mineral [30]. This exoskeleton at the lowest length scale is made up chains of α-chitin, a polymer

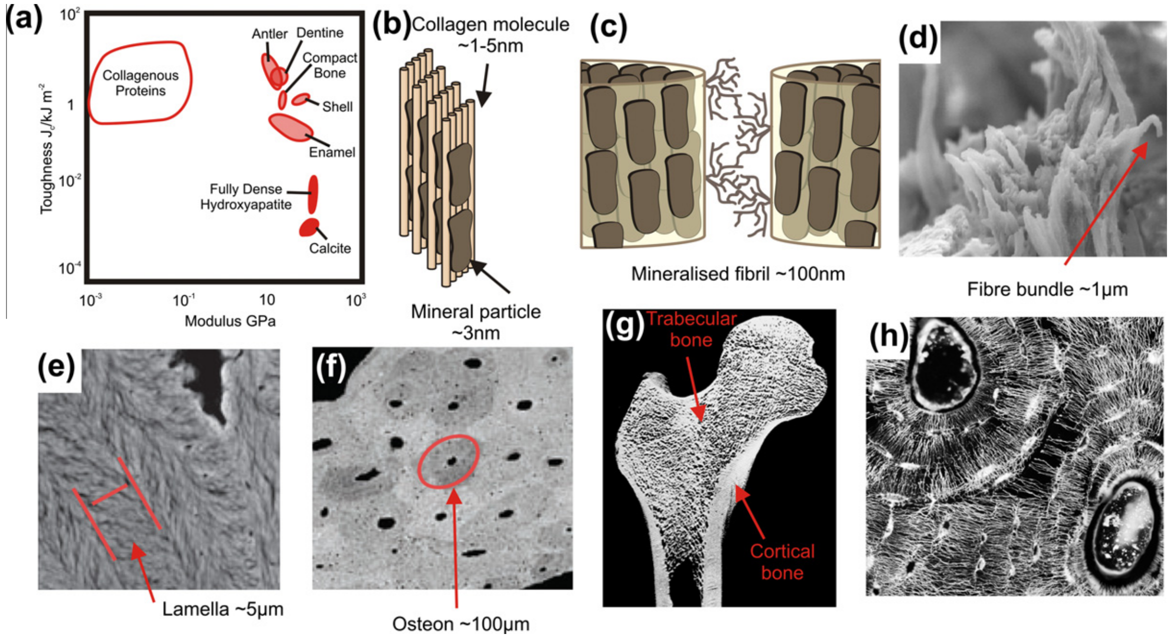

Figure 2. Multiple material architectures found in bone at different structural hierarchies. (a) The combination of the two main components of bone, mineral and protein, allows bone to achieve a stiffness approaching that of the mineral as well as having toughness approaching that of collagen. (b) Bone can be viewed as a fibre composite of ordered collagen molecules reinforced by plate-like mineral particles (c). These mineralized fibrils are "glued" together by non-collagenous proteins to make up (d) a mineralized fibre bundle. These bundles, in turn, are arranged into (e) lamellae. (f) Cortical bone contains osteons (highlighted by the red ellipse), consisting of concentric layers of lamellae, and makes up the outer part of the macroscopic bone itself. This is exemplified in (g), which is a cross-section through a human femur, showing both the cortical and the porous trabecular bone. (h) Bone is also an organ, as illustrated in this confocal image of two osteons, highlighting the canaliculi and osteocyte network. Part (a) is based on Ref. [2]; (b) and (c) are based on Ref. [4], (d)–(g) are from Ref. [32], reproduced by permission from the Royal Society of Chemistry; and (h) is from Ref. [20], with permission, copyright 2011, Elsevier. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

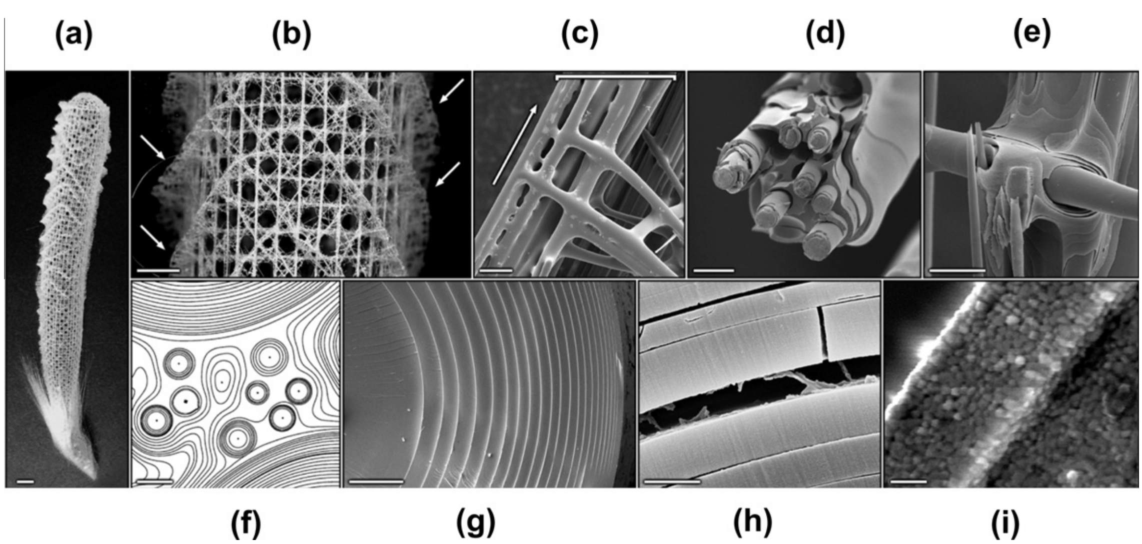

Figure 3. Multiple architectures found in the deep-sea sponge *Euplectella* sp. Skeleton. (a) Macroscopic architecture of the entire sponge skeleton (bar = 1 cm). (b) Reinforced square lattice making up the walls of the skeleton, showing diagonal bracing in every alternate square; arrows indicate orthogonal ridges (bar = 5 mm). (c) Detail of a single strut made up of a bundle of silica spicules; the arrow indicates the longitudinal direction of the strut (bar = 100 μm). (d) Acid-etched and fractured beam showing the ceramic fibre-composite structure (bar = 20 μm). (e) Image of an acid-etched joint, showing the fibre embedded in laminated silica layers (bar = 25 μm). (f) Contrast-enhanced image of a strut showing the multiple spicules embedded in a lamellar silica matrix (bar = 10 μm). (g) Details of the lamellar structure of a single spicule (bar = 5 μm). (h) Details of a fractured spicule showing evidence of a thin organic layer between the silica lamellae (bar = 1 μm). (i) A bleached surface of a cross-section showing the nanoparticles that make up each silica layer (bar = 500 nm). From Ref. [21], with permission from AAAS.

of N-acetylglucosamine (Fig. 4b and c). These chains are coated with protein (Fig. 4c) and bundle together to make larger chitin–protein fibres (Fig. 4d). The fibres themselves can be arranged in a parallel manner in

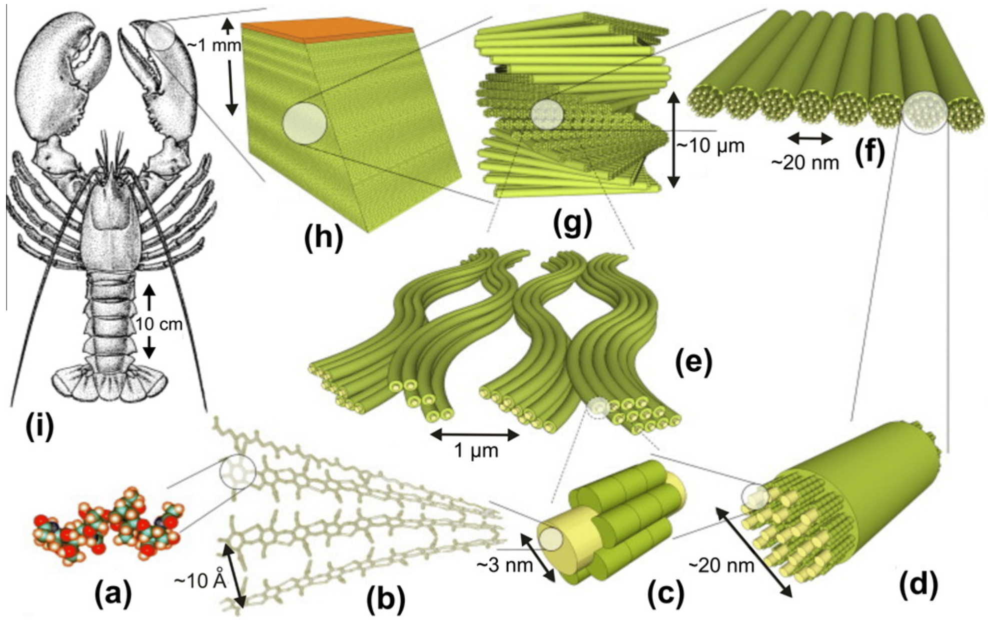

Figure 4. The cuticle of the arthropod *Homarus americanus* displays a variety of different architectures at multiple length scales. (a) N-acetylglucosamine molecules make up (b) chains of alpha-chitin. (c) These chains in turn form nanofibrils wrapped in protein, which bundle together to form (d) larger protein–chitin fibres and (e) mineralized honeycomb-like lamellae. These honeycomb lamellae and (f) lamellae containing more parallel-oriented fibres stack together to form (g) a "twisted plywood" structure making up (h) the multi-layered structure of the bulk cuticle of exoskeleton of the lobster (i). From Ref. [28], copyright 2011, Elsevier.

lamellae (Fig. 4f) or in a honeycomb (Fig. 4e). These layers are then stacked in a twisted plywood manner (Fig. 4g and h), making up the outer cuticle of the lobster (Fig. 4i) [28]. The cuticle is further reinforced by amorphous calcium carbonate. Such cuticles are moulted to allow the animal to grow. This presents a technical challenge, in that the new cuticle must first be flexible to allow growth of the animal after moulting, then must quickly mineralize to harden the structure against predators. To assist in this, some arthropods living in environments with low Ca bioavailability also produce specialized mineral stores called gastroliths, which are optimized to release Ca to the animal as fast as possible [31].

These four examples of biological materials illustrate the richness of structure that can be found at multiple length scales in nature. By combining relatively simple building blocks, fibres, polymers and minerals in an ingenious way, nature has been able to produce impressive multi-functional materials that may serve as inspirations for new artificial materials.

Acknowledgements

The authors are grateful to many colleagues and collaborators; in particular, we thank Ingo Burgert, Michaela Eder, Wolfgang Wagermaier and Richard Weinkamer for discussions.

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