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On the Materials Science of Nature's Arms Race

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Biological material systems have evolved unique combinations of mechanical properties to fulfill their specific function through a series of ingenious designs. Seeking lessons from Nature by replicating the underlying principles of such biological materials offers new promise for creating unique combinations of properties in man-made systems. One case in point is Nature's means of attack and defense. During the long-term evolutionary "arms race," naturally evolved weapons have achieved exceptional mechanical efficiency with a synergy of effective offense and persistence—two characteristics that often tend to be mutually exclusive in many synthetic systems—which may present a notable source of new materials science knowledge and inspiration. This review categorizes Nature's weapons into ten distinct groups, and discusses the unique structural and mechanical designs of each group by taking representative systems as examples. The approach described is to extract the common principles underlying such designs that could be translated into man-made materials. Further, recent advances in replicating the design principles of natural weapons at differing lengthscales in artificial materials, devices and tools to tackle practical problems are revisited, and the challenges associated with biological and bioinspired materials research in terms of both processing and properties are discussed.

1. Introduction

The progressive synthesis of differing fields of scientific and engineering endeavor has led to the emergence of a multitude of interdisciplinary topics that are so vibrant and promising to attract increasing research interest yet are still far from being fully exploited. Biological materials science stands out among these topics at the interface of the biological and physical sciences, representing the union of mechanics, physics, chemistry, and engineering (**Figure 1**).[1–3] The materials-science approaches of processing, properties, characterization, and theoretical modeling have been applied to probe biological materials created by Nature, as opposed to "traditional" man-made solids. Extensive research efforts have been directed to such materials, with emphasis on bamboo,[4,5] trees,[6–8] mollusks,[9–15] arthropods,[16–21] birds,[22–27] fish,[28–34] mammals,[35–43] and human beings,[44–53] motivated not only by their unique structures and properties/functionalities, but also by the salient mechanisms and underlying design principles that account for their long-term perfection.

Biological systems represent how a wide diversity of generally composite materials can be developed to best fulfill their specific demands using a fairly small palette of chemical constituents, often with relatively meager intrinsic properties but which are environmentally friendly and readily available. The combination and arrangement of these constituents in biological materials are ingeniously modulated from molecular- to macrolevels to create complex, multiple lengthscale, hierarchical architectures with abundant internal gradients and interfaces.[8,38,54–61] Such designs enable marked enhancements in the properties of these materials, sometimes by orders of magnitude compared to those of their constituents (**Figure 2**a,b).[1–3,38,62–64] In light of the intricacies of Nature's design of materials, scientific endeavor in the form of biomimetics and bioinspiration has begun to offer significant potential in providing creative solutions to developing unprecedented combinations of properties and functionalities in synthetic materials.[2,3,65–74] In this respect, aside from the inherent difficulties in processing synthetic materials in the image of Nature, any success in bioinspired materials' design rests on a sufficient knowledge about the structure and properties of biological systems and, in particular, the underlying rationales and design motifs. Accordingly, to bridge the gulf between biological materials science to bioinspiration, biomimetics, and the actual processing of bioinspired materials, three sequential stages of endeavor are necessary (Figure 1):

1) Characterizing the structure and properties/functionalities of biological materials, especially under their specific physiological conditions, and clarifying the structure–property relationships which serve as the basis for any attempt to mimic them.
2) Understanding the mechanisms responsible for their unique properties/functionalities and extracting the key design principles conferring such mechanisms—it is these principles that need to be translated into bioinspired design as opposed

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to a rigid replication of the naturally occurring structures per se.[65,67]

3) Learning from Nature by implementing the biological principles in synthetic materials and components to improve their performance so as to better meet the requirement for practical application, and (perhaps the most difficult part) developing processing pathways to create multiscale hierarchical architectures, coupled with gradients, that allow for a more effective control of materials characteristics to accomplish it.

Among the large diversity of biomaterial systems, one critical feature for most organisms is the means of attack and defense. Indeed, natural weapons play a role principally for these multiplex mechanically stringent applications, e.g., capturing and killing prey, feeding, fighting, self-defense against predators, which are vital for survival and consequently have been optimized within their environmental constraints for mechanical efficiency.[30,31,75–79] Unique combinations of mechanical properties have been developed in these materials so that they can maximize the offence exerted to opponents, while at the same time maintaining sufficient persistence by minimizing damage to themselves. Both these functional features are crucial for any weapon yet tend to be mutually exclusive in a single material, i.e., an efficient attack in biological systems frequently results from the use of considerable force and velocity which invariably increases the risk of self-injury.

In this scenario, the natural weapons represent a vast treasure trove of discoveries for fascinating structures, properties/functionalities, and design motifs created by Nature, which may present abundant new knowledge in materials science. Of still further significance is their promising role as a rich source of inspiration for man-made systems, specifically those for structural applications where significant impact and wear resistance are desired. Unfortunately, such materials remain largely to be explored, especially when compared to the wealth of information on their opponents, i.e., the protective armors that provide passive defense to organisms, such as the mollusk shells,[9–12,14,15,61] fish and pangolin scales,[28–34,41,80,81] and the turtle carapace.[82–84] In particular, to develop a high attack efficiency in addition to a protective role, the natural weapons have evolved a series of unique designs that distinguish them from Nature's armors and other structural materials. Numerous hidden mechanisms and design principles associated with such weapons still need to be identified, validated, and possibly implemented in the bioinspired materials of the future.

Here, we revisit the critical structural and mechanical designs employed by naturally evolved weapons in pursuing their high mechanical efficiency in Nature's evolutionary arms race by taking selected materials as examples in the framework of a classification of such weapons into ten different groups. The common materials-design strategies towards an outstanding synergy of offence and persistence (rapid repair) are analyzed and extracted from these weapons. Representative state-of-the-art progress in man-made systems, where such strategies have been replicated, is also presented. Finally, we discuss the main challenges and potential opportunities associated with natural weapons in biological and bioinspired materials research and outline a promising future perspective for this emerging field.

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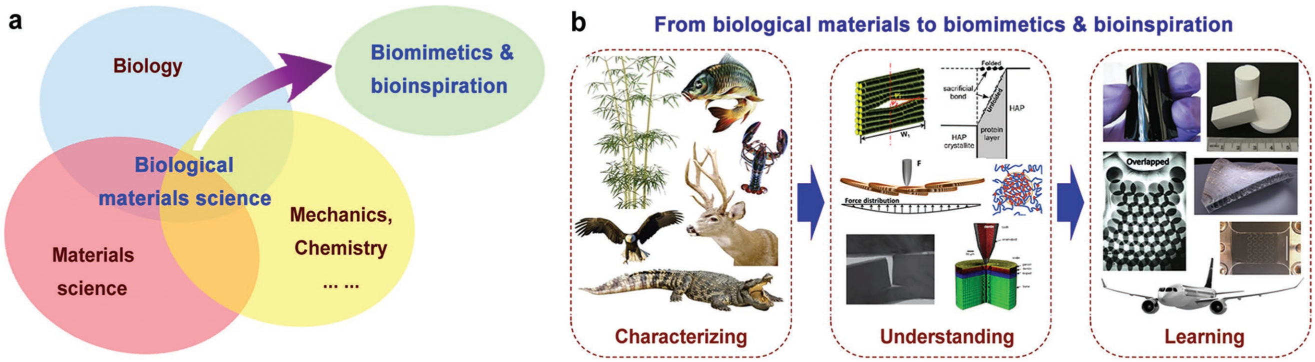

Figure 1. Biological and bioinspired materials research. a) As a rapidly growing interdisciplinary frontier, biological materials science, where the materials science approaches and principles are utilized to investigate biological material systems and extract the creative design strategies of Nature, breaks the traditional boundaries between the physical and biological sciences by combining endeavors in mechanics, chemistry, physics, engineering, etc. b) By seeking lessons from Nature, inspiration can be engendered for the design and development of new materials and functionalities. Three sequential stages, i.e., characterizing (biological systems), understanding (the underlying mechanisms and principles), and learning (from Nature by replicating biological strategies in man-made systems), are involved in the research from biological materials science to biomimetics and bioinspiration.

2. Structural and Mechanical Designs of Naturally Evolved Weapons

The differing environmental challenges faced by various organisms have led to a considerable diversity of their evolved weapons,[75–79] most of which are distinguished by an impressive mechanical efficiency, i.e., the mechanical properties of natural weapons and other biological materials are comparable to those of many current engineering materials (Figure 2a,b).[2,62–64] This makes such natural materials rather

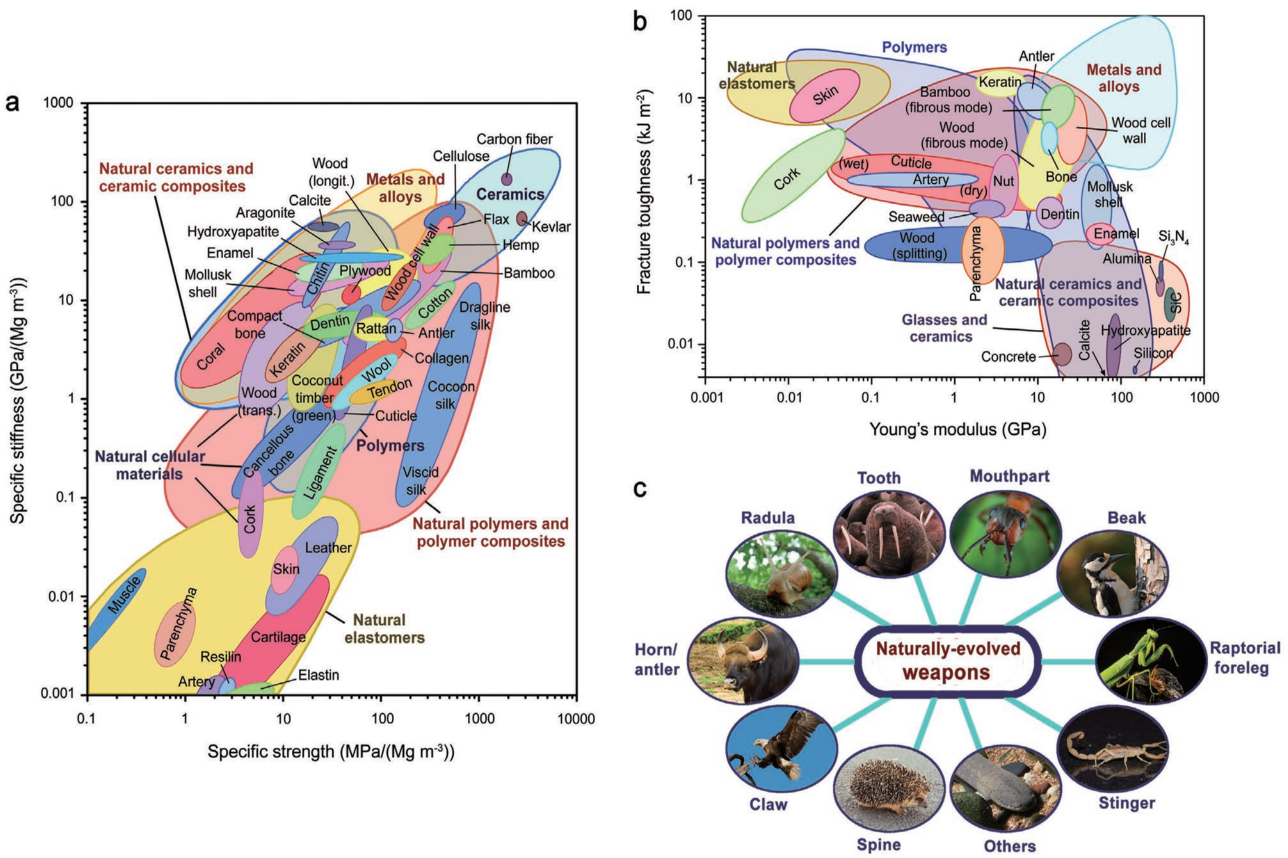

Figure 2. Mechanical efficiency of biological materials and classification of natural weapons. a,b) Ashby images of the mechanical properties for the naturally evolved weapons and other biological materials as compared to those of synthetic ones.[62–64] a) The specific values (i.e., normalized by density) of stiffness against strength. b) The fracture toughness plotted against Young's modulus. c) Ten different groups of naturally evolved weapons and their respective typical examples. a,b) Reproduced with permission.[63] Copyright 2004, Taylor & Francis.

remarkable considering the limited choice of constituent materials in Nature, their often rather meager intrinsic properties, and the mild conditions and economical energy input for materials synthesis.[24,36,85–87] However, during the long-term evolutionary arms race, similar solutions arise among different animal species, signifying some degree of convergent evolution.[78,79]

We propose here a classification of natural weapons into ten distinct groups (Figure 2c), where within each class there are analogous form, structure, and functionality. The principal designs in their structure and resulting mechanics underlying their performance are presented in the following sections through representative examples.

2.1. The Tooth

The tooth is the most common weapon developed by vertebrates mainly for breaking down food, hunting (particularly in carnivores), self-defense, fighting (especially in the case of the elongated tusk in certain mammals), and so forth. The mechanical properties of teeth originate primarily from two distinct parts, specifically the less-mineralized dentin, which represents the main body of the tooth, and the highly mineralized enamel or enameloid—two tissues that are formed in differing modes in different animals yet are quite similar in their final structures,[88] which covers it for wear and impact resistance.[2,30,38,45,48] Graded interfaces are employed to join the dentin and enamel/enameloid and to fix them to the underlying substrate.[48,58,89]

The ingenious design of the tooth as a weapon is perfectly represented by shark (*Isurus oxyrinchus*) teeth which have evolved into an intricate structural hierarchy (**Figure 3**a).[90–92] The enameloid is composed of elongated fluoroapatite crystallite bundles, a few micrometers in diameter, which have a nanoscale organic envelope in between. The fiber-like crystallites have a diameter of 50–80 nm and length exceeding 1 µm. This enameloid region is covered by an outermost shiny layer and connects to the dentin through a rough interface where the constituents are intertwined to result in a graded transition between them. Specifically, three types of bundles, oriented respectively in the axial, radial, and circumferential directions, are formed in the bulk enameloid and interwoven into a textured architecture. Additional to the high degree of mineralization, the geometric sharpness and strong axial alignment of the mineralized bundles, which are rarely seen in nonweaponized materials, generate a high attacking efficiency for the teeth. The toughness of the enameloid, on the other hand, results mainly from its complex structural hierarchy and abundant interfaces. This differs from the enameloid-containing armor materials (e.g., *Polypterus senegalus* fish scale[29,30]) that derive their damage tolerance from mechanisms such as preferred circumferential cracking of the enameloid and extensive plastic deformation in its less-mineralized foundation—both may cause vital damage to the teeth. Additionally, the fluoridation of apatite helps improve the durability of teeth as it reduces water solubility by orders of magnitude.[93,94] Such multiscale structural regulation endows the shark tooth with a powerful attacking potency to easily lunge and tear into prey without self-damage.[95]

2.2. Mouthparts

Lacking the existence of teeth, invertebrates have broadly developed an oral appendage or mouthpart that is frequently fused by tooth-like structures as a weapon to grasp, cut, or crush their food and fight against enemies. The mouthpart appears as mandibles in arthropods and jaws in worms,[96–101] yet takes a modified form of stylets for piecing plant or animal tissues and sucking their fluids in some insects such as bugs, mosquitos, and lice.[102,103] In contrast to the vertebrate tooth, which principally moves vertically, the mouthpart features a freedom of movement in the horizontal plane for mandibles and jaws or following the forward–backward manner in the case of stylets.

The crayfish (*Cherax quadricarinatus*) mandible is a prime example of such weapons where the chemical composition and structure are elaborately designed (Figure 3b).[96,99,101] A hard cap composed of highly crystalline fluorapatite prisms, reminiscent of the vertebrate enamel, is interdigitated with a soft base of chitin reinforced by amorphous minerals through a graded interface where the mineral composition transforms from amorphous calcium phosphate to amorphous calcium carbonate. The fluorapatite crystals are co-aligned in the crown with their *c*-axes normal to the outer surface of mandible to maximize stiffness along the loading direction for an efficient load transfer to the opponents. The chitin fibers are transversely oriented in the form of a twisted plywood (Bouligand-type) structure in the basal region, yet gradually radiate along the radial direction towards the interface with the apatite layer—an adaptation that creates graded mechanical properties for enhanced protection.[104] This is additionally accompanied by an increase in the mineral content. Such chemical and microstructural gradients allow the mandible to combine a high stiffness, hardness, and wear resistance from the exterior with an increasing damage tolerance towards the interior—two characteristics that principally contribute both to offence and persistence, yet play a synergistic role to enhance the performance of the weapon.

2.3. The Radula

The radula is a chitinous ribbon armed with numerous minute teeth and is typically used as a flexible weapon system by mollusks to collect, scrap, or cut their food in a way similar to either a rake or a rasp. The radular teeth, unlike normal vertebrate teeth, are assembled into a number of self-similar rows as on a conveyor belt with their morphologies adapted among different species based on the food sources.[105–109] The distinct operation mode of radula requires its tooth material to be highly resistant to abrasion. Indeed, the radular teeth of chitons (*Cryptochiton stelleri*) that function to graze for algae on rocky substrates represent the hardest and stiffest biological materials reported thus far (Figure 3c).[106,109] Each radular tooth in its mature state consists of a hypermineralized cap composed of organic-encased nanoscale magnetite rods and an inner core enriched in weakly crystallized iron phosphate and organic phases. The mineral rods are highly oriented parallel to the tooth surface and exhibit a smaller diameter on the leading edge compared to the trailing edge, providing local strength optimized for specific

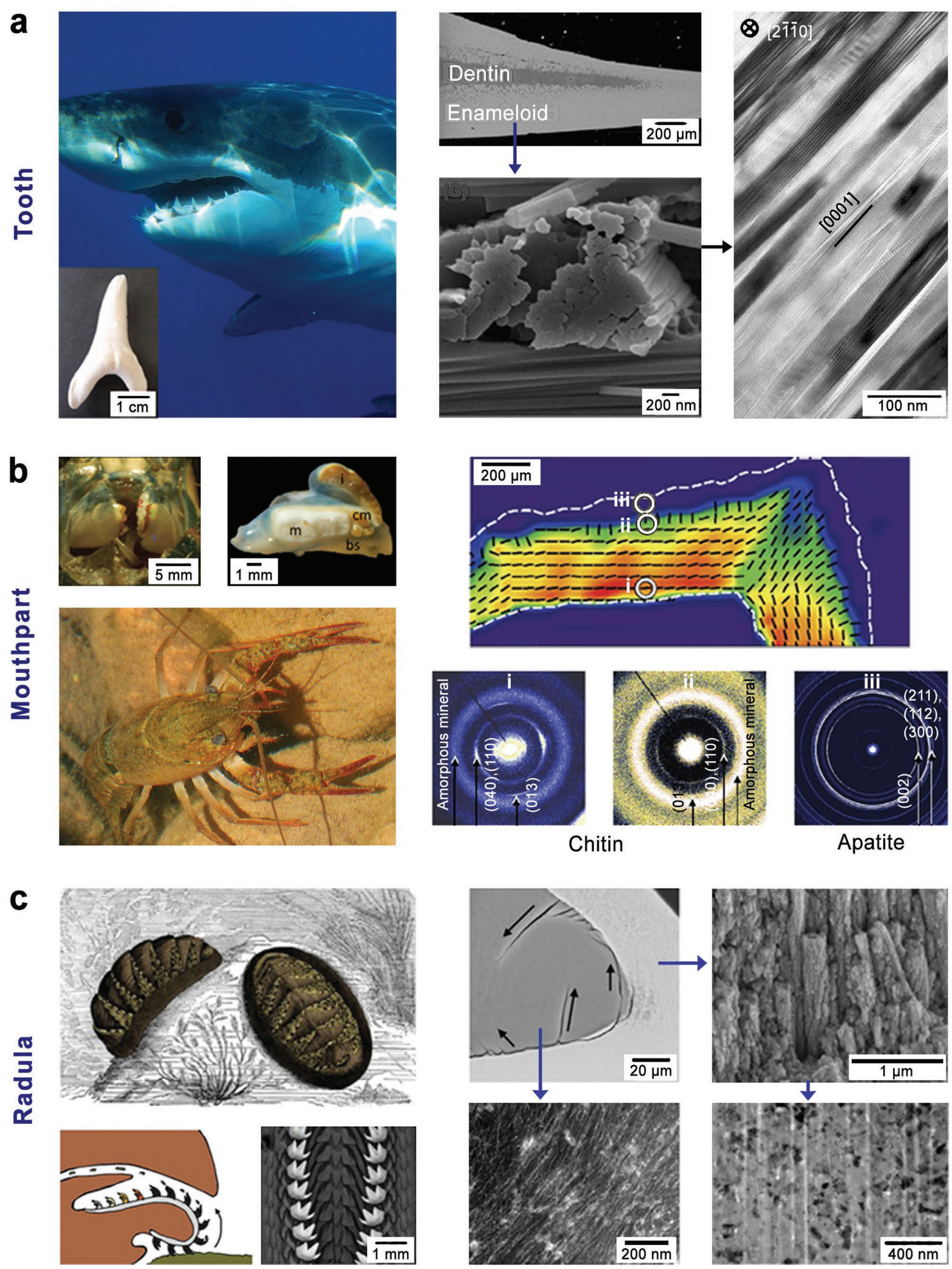

Figure 3. Structural and mechanical designs of the tooth, mouthpart, and radula. a) The hierarchical structure of the shark tooth from the macro- to the nanoscale.[90–92] b) The morphology, constituents and their graded distribution, and orientation of the crayfish mandible as revealed by microbeam scanning wide-angle X-ray scattering.[99,101] c) The morphology and operation mode of chiton radula and the hierarchical structure of the radular tooth.[106,109] a) Scanning electron microscopy (SEM) image of the entire tooth: Reproduced with permission.[90] Copyright 2012, Elsevier; SEM image of enameloid: Reproduced with permission.[92] Copyright 2014, Elsevier; transmission electron microscopy (TEM) image: Reproduced with permission.[91] Copyright 2014, Wiley-VCH. b) Microscopy images and diffraction patterns of crayfish mandible: Reproduced with permission.[99] Copyright 2012, Nature Publishing Group. c) Microscopy images of chiton radular tooth: Reproduced with permission.[106] Copyright 2010, Elsevier; schematic of rasping motion of chiton radula: Reproduced with permission.[109] Copyright 2014, Wiley-VCH.

loading conditions. The higher mineralization of the leading edge leads to a hardness gradient across the tooth which helps create a self-sharpening condition.

Despite their independent occurrence over broadly divergent organisms, the three weapon groups of the tooth, mouthpart, and radula appear to have developed remarkably similar strategies to enhance their mechanical performance, suggesting a degree of evolutionary convergence in Nature's creation of high-quality weapons. This is specifically represented by the combination of a hard and stiff shell, which functions principally to provide offence, with a soft, yet more compliant, base that favors a good persistence achieved through a series of gradients and structural hierarchy. Such designs are adopted to create remarkable attacking efficiency of the weapon, in addition to enhancing protection, strategies that appear to be more creative than the functions of Nature's armors and other structural materials.

2.4. The Beak

The beak, as a union of two bony projections enveloped by a thin keratinous layer of rhamphotheca, is an external structure in birds used mainly for such mechanical functions as gathering and eating food, manipulating objects, and killing prey. It also represents a form of weapons, termed rostrum, similar to that developed in a wide variety of other animals, e.g., cephalopods, where the squid beak is known for its notable hardness and large stiffness gradients,[110,111] cetaceans, dicynodonts, and turtles. The bird beak provides an illuminating insight into how sufficiently high rigidity and robustness can be achieved in materials with a minimum weight penalty—which is critical for flight—by utilizing expert designs.[22,23,26,27,112,113]

A good example here is the red-bellied woodpecker (*Melanerpes carolinus*) beak which is used to penetrate trees—a beak that functions more like a weapon as compared to the chicken and toucan beaks that are used for grabbing food or crushing fruit (**Figure 4**a).[23,26] The keratin scales in the rhamphotheca are more elongated along the longitudinal direction than in the chicken and toucan beaks, in order to achieve high friction to dissipate more impact energy. The scales are connected through a suture structure—a feature that provides extra stiffness and strength[112]—with a narrow gap to admit energy dissipation via local shearing between the scales. An additional characteristic that distinguishes the woodpecker beak from less-weaponized beaks is the markedly lower porosity of the boney core which helps strengthen the beak and focus the stress waves that it can create. Such designs make the woodpecker beak a potent weapon to exert considerable stress to the tree while effectively absorbing impact energy and avoiding compressive buckling in the loading direction. This design is far more efficient than other natural materials, such as the turtle carapace[82–84] and bird feather rachis,[25,27] which possess a somewhat similar form, i.e., porous core enveloped by dense shell, but which function only to resist bending or impact along the orthogonal direction.

2.5. Horns/Antlers

A horn is a pointed projection on animal's head used mainly by Antilocapridae, Bovidae, and some beetles (such as Dynastinae[77–79]) as a weapon to defend themselves from predators and fight for territory, dominance, or mating priority. The horn of mammals consists typically of a bony core covered by a sheath of keratin and other proteins,[40,114–118] except for the rhino horn that is fully made of keratin.[87,119] Antler is a similar instrument as horn protruding from the frontal skull, but is unique to cervids and, in contrast to the horn which is permanent, is often branched and sheds annually. The horn and antler are distinguished by an extraordinary damage resistance as they are usually subject to considerable impact loading and bending moments.[120,121] Additionally, they display a remarkably high ability to absorb energy to minimize the transmission of impact loads to the animal's head.

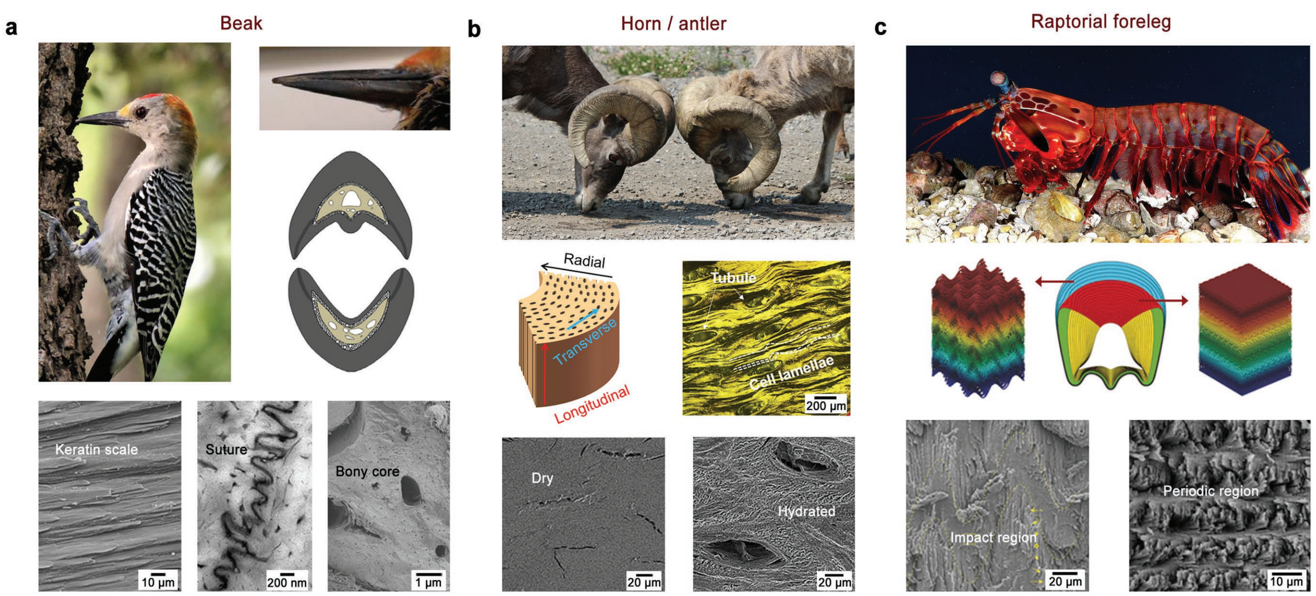

Figure 4. Structure and mechanics of the beak, horn/antler, and raptorial foreleg. a) The morphology and unique structural characteristics of woodpecker beak.[23,26] b) The structure and deformation mechanisms of tubule collapse and self-recovery of bighorn sheep horn in dry and hydrated states under impact along the radial direction.[115,118] c) Schematic illustrations and images of the helicoidal and herringbone structures of the inner periodic and outer impact regions in the stomatopod dactyl club.[20,129] a) Reproduced with permission.[23] Copyright 2014, Royal Society Publishing. b) Microscopy images: Reproduced with permission.[118] Copyright 2017, Elsevier. c) Microscopy image of the helicoidal structure: Reproduced with permission.[20] Copyright 2012, American Association for the Advancement of Science; schematics and microscopy image of the herringbone structure: Reproduced with permission.[129] Copyright 2016, Wiley-VCH.

The horn of bighorn sheep (*Ovis canadensis*) is a prime example where such high performance is generated through expert mechanical designs (Figure 4b).[115–118] Tubules with an elliptically shaped cross section extend along the longitudinal direction of the horn and are dispersed within a laminated structure formed by keratinous cells. Such structure differs from that of the horse hoof—another biological material with tubular structure—where the tubules are aligned parallel to the loading direction to resist compression.[24,87] The horn keratin is composed of α-helical crystalline intermediate filaments embedded in an amorphous keratin matrix which is sensitive, and can respond to hydration. Both stiffness and strength of the horn increase significantly with increasing strain rate, leading to enhanced resistance to impact loading. The radial direction, which is the direction of impact loading, exhibits the highest energy absorption through tubule collapse—a deformation mechanism that allows the horn to sustain considerable strain without fracture. Moreover, the deformation can be recovered under a hydrated state as water can aid repair of the keratin matrix, which enables the horn to withstand multiple blows during ramming.

2.6. The Raptorial Foreleg

The raptorial foreleg represents the leg segment or appendage of arthropods that has been greatly adapted for catching, gripping, or smashing their prey. Such weapons are equipped by various insects in the families of Mantidae, Mantispidae, Belostomatidae, Nepidae, etc., where the praying mantis is the most widely known for its spiked foreleg,[122,123] and some crustaceans (e.g., the mantis shrimp[20,21,124–129]). The mechanical robustness of raptorial foreleg is prominent as it is frequently used to break armors made of the same material, e.g., the mantis foreleg versus the cicada exoskeleton, both of which are chitinous, or even stronger components, e.g., the mantis shrimp foreleg versus the abalone shell.

The exquisite design of raptorial foreleg is represented by the hammer-like dactyl club of a stomatopod (*Odontodactylus scyllarus*) (Figure 4c).[20,21,125–129] The club exhibits a mineral gradient with fluorapatite substituting amorphous apatite towards the impact surface. The outer region is highly mineralized, comprising crystalline fluorapatite nanorods that are preferentially oriented towards the impact surface. This leads to a high surface hardness and stiffness that enable an effective transfer of impact momentum to the prey. The attacking efficiency can be further amplified by the saddle which acts like a spring to store and release elastic energy. On the other hand, the inner region is composed of partially mineralized chitin fibers that are arranged into a helicoidal structure, resulting in an oscillation of local mechanical properties and twisted paths for any crack propagation. Such structure is modified, by taking a triangular waveform, into a well-defined herringbone pattern in the impact region and covered by a thin layer of isotropic apatite nanocrystals—an adaptation that affords efficient stress redistribution and energy dissipation. The damage tolerance of the club is additionally enhanced by the quasi-plastic nature of the impact region from the interfacial sliding and rotation of fluorapatite nanorods and the strain-hardening behavior of the bulk associated with microchannel densification. The integration of these designs enables simultaneously enhanced offence towards the surface and improved persistence towards the inner region, making the club fairly formidable to smash its adversary, e.g., mollusk shells, fish skulls, and crab exoskeletons, without inducing noticeable self-damage.

2.7. Claws

The claw is a hooked, pointed appendage growing at the end of a finger or toe in amniotes (e.g., mammals, reptiles, and birds). Here the term "claw" is also used to represent the homologous but plate-like nail in primates and a few other mammals, and the pincer-like chela that has a similar curved shape terminating certain limbs of such arthropods as crabs, lobsters, and scorpions.[47,130] The claw generally suffers a bending force from downward motion in service either as a weapon for hunting prey and self-defense or as a tool for digging, grooming, climbing trees, etc. The claws of mammals are primarily composed of α-keratin, while those of reptiles and birds comprise mainly β-keratin. Although seldom containing minerals, the keratin is highly cross-linked by forming abundant disulfide bonds between the polypeptide chains and between the keratin fibers and amorphous matrix, making the keratin among the toughest biological materials.[24,87,131] The claw of tetrapods typically consists of a hard exterior unguis covering a soft subunguis layer with the keratin fibers arranged in different orientations, reminiscent of the graded nature of tooth.[47,130,132]

Aside from its microstructure, the macrogeometry of the claw is further adjusted to reduce the risk of mechanical failure while still maintaining a high attacking potency—this is exemplified by the tiger claw which has a fatal power to scratch into both soft tissues and bones even to cause the death of victim (**Figure 5**a).[133–135] The claw exhibits a concave contour following logarithmic spirals. Such shape helps produce a more constant stress state across the claw under its service condition, i.e., no point on the claw is more susceptible to failure than any other, and so no superfluous material is retained. This contrasts with the circular arches in conventional engineering design of hooks that tend to cause unfavorable stress concentration near the pole. The geometric adaptation of claws is also represented by their differing shape among different animals which is associated with their specific functions. For example, an enhanced clinging and climbing performance of lizards is usually featured by a higher degree of curvature and greater height at the base of claw.[136]

2.8. Stingers

A variety of animals, typically arthropods, have developed a sharp and in some species barbed organ, namely the stinger or sting, which is normally at the rear of their body and often coupled with one or more venom glands, to pierce the epidermis of a rival. Such incisive weapons are also used by some nonarthropods with similar function, e.g., the modified dermal

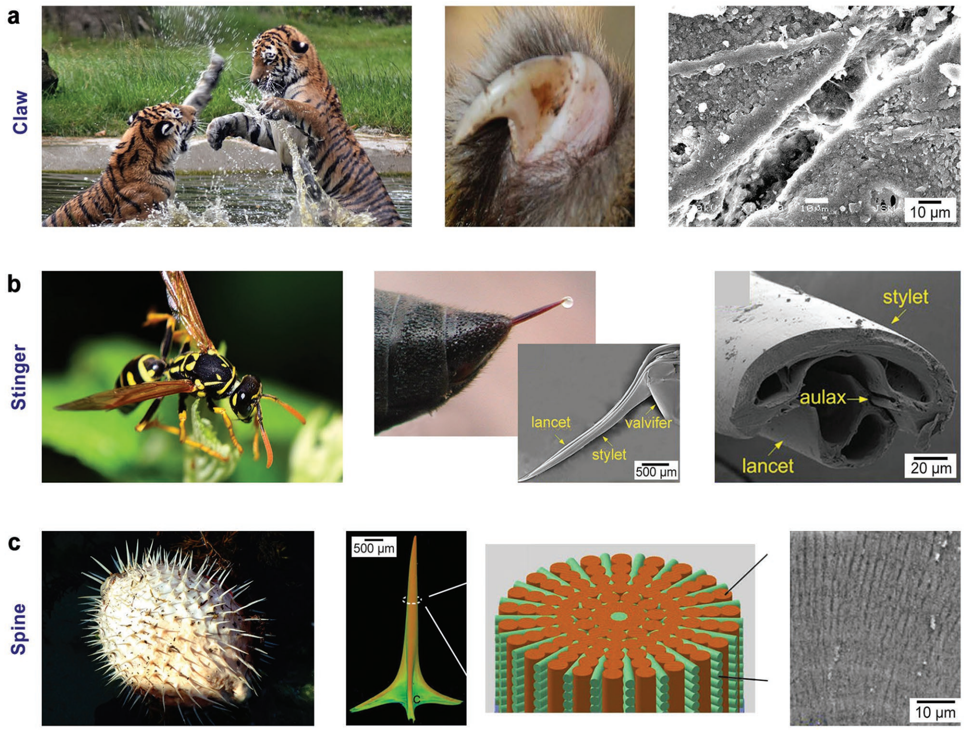

Figure 5. Claw, stinger, and spine as naturally evolved weapons. a) The geometry of a tiger claw and its lethal attacking power as revealed by the scratching gouge into a bovine femur bone.[134,135] b) The morphology of a wasp sting with a venom droplet and images of its architecture.[141] c) The morphology of a porcupine fish spine and a schematic illustration and image of its structure.[150] The graded density across the spine is depicted using a varying color with the regions of the highest and lowest densities marked, respectively, in red and blue. a) SEM image: Reproduced with permission.[134] Copyright 2013, The Authors, published by PLOS. Image of tiger claw: Reproduced with permission.[135] Copyright 2014, Elsevier. b) Microscopy images: Reproduced with permission.[141] Copyright 2015, The authors, published by The Company of Biologists. C) Microscopy images: Reproduced with permission.[150] Copyright 2017, Elsevier.

denticle of the stingray and the cnidocyte tentacle of jellyfish, which are also referred to as stings. The injury inflicted by a stinger can be strikingly amplified by the introduction of venom which may cause severe allergic reaction or systemic symptoms that lead to intense pain and even death.[137,138] The stinger has been optimized at micro- to macroscales to permit easy penetration and extraction (that can be used repeatedly) with respect to the target tissue, with effective venom injection, while avoiding problems of compressive buckling.[139–142]

The paper wasp (*Polistes* sp.) sting, which features a curved shape and a hollow structure comprising a stylet and two slightly barbed lancets, is an illustrative example of such designs (Figure 5b).[139,141] The lancets, as each in turn is thrust forward, saw through the victim's epidermis and are anchored in place by their barbs. These barbs may help reduce the penetration force by inducing stress concentration in the tissue and squeezing out tissue fluids as lubricants.[143] A spiral geometry is utilized by the lancets to hide its barbs inside the stylet and reduce the transverse span of the sting such that the dragging force during extraction is minimized. Additionally, the stylet adopts a reinforcing rib on the ventral side to improve its buckling resistance under axial compression. A flexible connection between the stylet and lancets is realized through a sliding–interlocking mechanism via a rail-groove structure, enabling a cooperative motion of the two parts.

2.9. The Spine

The spine is a hard, needle-like structure employed by a broad range of animals, both vertebrate and invertebrate, mainly as an active-defense mechanism to repel or retaliate against potential predators. Such a type of weapon shows a large diversity among different taxa,[143–150] e.g., the bristle of caterpillar, the dorsal spine of bony fish, the calcareous spicule of sponge, and the quill of porcupine, and tends to be conspicuous in many species to advertise its danger and defensive power.[151] The spine in mammals consists typically of a foam core covered by a hard keratinous sheath, as represented by the hedgehog prickle and porcupine quill.[145,149] The foam is closed-celled and tightly bonded to the cortex and, in some species (such as African porcupine), is strengthened by longitudinal stiffeners, leading to enhanced axial stiffness and compressive buckling resistance. The American porcupine quills have developed barbs on the surface to allow for easy penetration and difficult removal with respect to the target tissue.[143,149] Such a function differs from nonweaponized biological materials where the foam-filled structures are often used to resist impact and bending along the orthogonal direction.[8,25,37–39,74]

In comparison, a markedly different design is involved in the spine of porcupine fish (*Diodon holocanthus* and *Diodon hystrix*), which is a nanocomposite of hydroxyapatite and (hydrated) collagen (Figure 5c).[150] These spines display a graded mineralization level with the spinous section most mineralized and the base least mineralized, leading to a graded transition from enhanced offence of the tip to improved compliance towards the base. The mineralized collagen sheets composed of longitudinally oriented fibrils are stacked along the radial direction of the spine. Such sheets are interwoven with unmineralized layers of radially oriented fibrils and connected by mineralized bridges in between. The preferred orientation of laminated features (along the longitudinal direction) helps maximize the axial stiffness of the spine for easy puncturing of predators; on the other hand, the existence of abundant radial interfaces affords additional toughness by promoting the deflection of cracks.

2.10. Others Weapons

Nature has evolved a variety of other attacking strategies, beyond the ones described above that exploit principally the mechanical properties of materials from the organisms per se, based on the sticky tongue, water jet, cavitation bubble, venom, chemical, electricity, and cobweb, to name but a few (**Figure 6**).[78,79,137,152–163] These represent a multitude of nonconventional weapons that make use of functions far more than merely mechanical efficiency. Formidable offence as that attainable by mechanical forces can also be generated using these approaches yet in a more ingenious manner. The electric eel is an excellent case in point that can shock an alligator to death by its lethal discharge.[161,162] Such weapons often encompass a series of intriguing biological processes, e.g., the chemical explosion of bombardier beetle and the silk-spinning of spider.[154,157,158,163] These processes may be enlightening to artificial design and the processing of materials, as represented by the inspiration from spider for the spinning of high-strength synthetic fibers.[164–169]

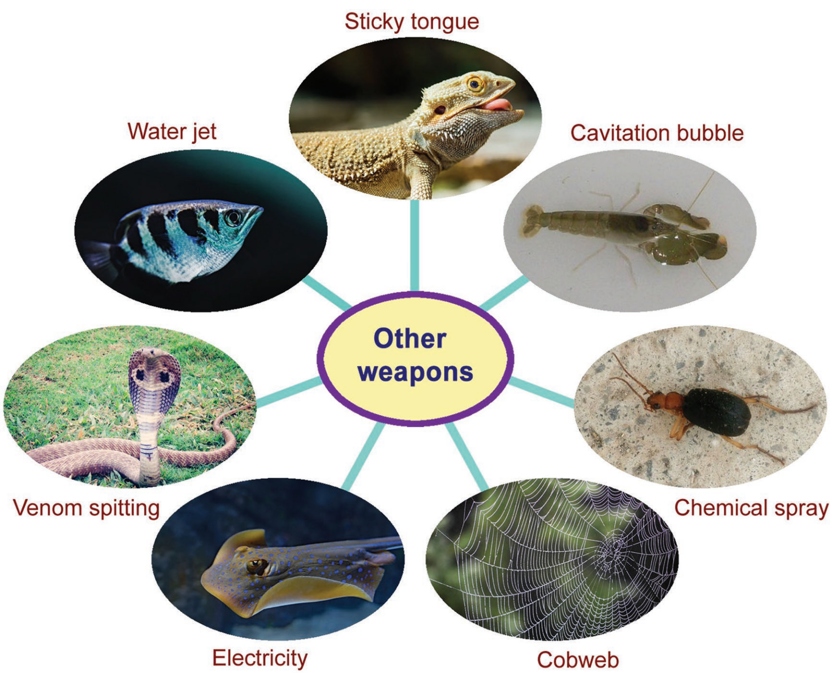

Figure 6. Natural weapons utilizing functions beyond mechanical efficiency. Typical examples of natural weapons that create their offence by utilizing distinct functionalities, which are more than just based on their mechanical properties, include the sticky tongue of the lizard and the anteater, the water jet projected by the archer fish, the cavitation bubble produced by the snapping shrimp, the venom spitting employed by the spitting cobra, the superheated chemical spray of the bombardier beetle, the electric discharge produced by the electric ray and eel, and the cobweb used as a tangible tool by spiders.[78,79,137,152–163] Such weapons aptly demonstrate a fine diversity of strategies and an ingenious manner that organisms have adopted to address their long-term evolutionary arms race.

3. Strategies towards Efficient Offence and Persistence

Current man-made materials derive their properties and functionalities largely from a vast repertoire of chemicals, and generally exhibit a definitive composition and uniform structure with well-defined properties.[170,171] Biological systems, as represented by naturally evolved weapons, provide an alternative approach that materials can be made strong and damage-tolerant using limited components and low-temperature processing. Nature's mechanical weapons are invariably complex composite materials comprising structural hierarchies, gradients, and graded interfaces to create remarkable compositional and structural heterogeneities.[2,72,172–174] Additionally, Nature's materials are often smart in that they sense and respond to changes in their living environment and specific conditions, in order to undergo self-adaptation, self-healing, or self-replacement of broken parts using fresh ones to retain their function.[175–183] An example here is the shark which can replace lost teeth within a single day.[175,176] The result is a subtle coupling and balance of efficient offence and sufficient persistence in these weapons—two properties that are highly favorable but often appear contradictive in many synthetic systems. In terms of materials design, the generation of materials for offence results mainly from such mechanical properties as stiffness, strength, and hardness, while the property of persistence is generated more from the resilience, fracture toughness, plasticity and resistance to impact, wear, and fatigue. However, Nature's approach recognizes that many properties primarily originate at differing lengthscales and from specific locations. Instead of using abundant chemical components, as in engineering systems, natural weapons have developed a series of strategies, particularly through architectural construction and developing gradients, in their quest for high functional performance, so that such unusual combinations of properties can be attained.

As exemplified by the resemblance between mosquito stylet (mouthpart) and bee sting (stinger),[102,103,139,141] remarkably similar motifs have been utilized among different weapon groups, representing long-term convergent evolution, but largely independent adaptation of organisms to their respective arms race. From the materials-science perspective, several common principles underlying the designs of the largely diverse weapons can be extracted, as discussed in the following sections (**Figure 7**a).

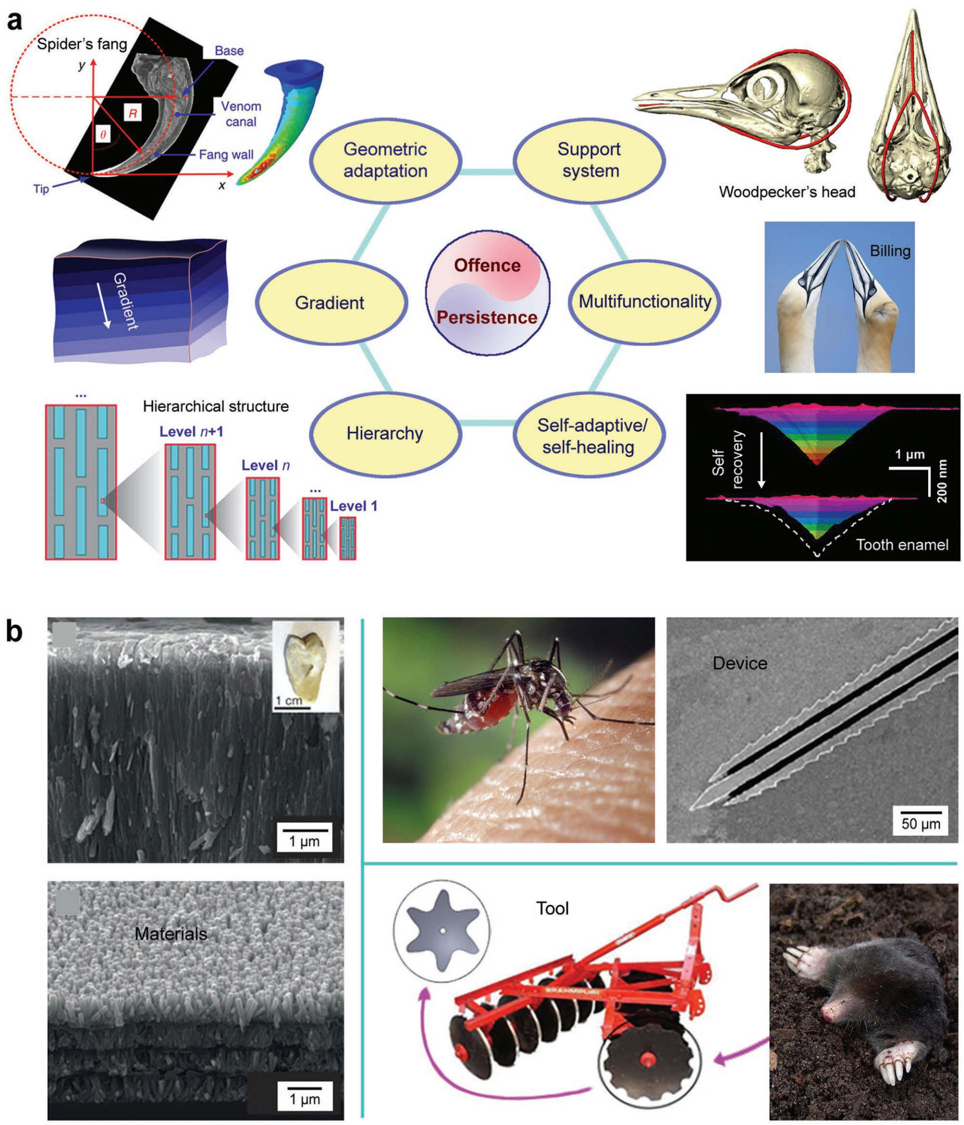

Figure 7. Extracted design strategies and lessons from natural weapons. a) Typical examples and schematic illustrations of the common design strategies used by diverse naturally evolved weapons to achieve a combination of efficient offence and sufficient persistence.[55,174,184,189] b) Representative examples for the translation of the designs from natural weapons to man-made materials, devices, and tools at differing lengthscales by implementing, respectively, the inspiration from tooth enamel, mosquito stylets, and mole paw.[199,201,203] a) Microscopy image of a spider's fang: Reproduced with permission.[184] Copyright 2014, Nature Publishing Group; schematic of hierarchical structure: Reproduced with permission.[55] Copyright 2006, Springer; microscopy images of woodpecker's head: Reproduced with permission.[189] Copyright 2016, IOP Publishing Ltd. b) Microscopy images of tooth enamel and enamel-inspired materials: Reproduced with permission.[199] Copyright 2017, Nature Publishing Group; microscopy image of microneedle: Reproduced with permission.[201] Copyright 2008, Wiley-VCH.

3.1. Geometric Adaptation

The macro shape and geometry of natural weapons are well optimized, e.g., via appropriate size, sharpness, barbs, curvature, and taper,[78,90,133,143,184] to support distinct biomechanical functions. This is represented by the long, pointed canine tooth of mammals which is used, while avoiding severe stress concentration,[176,185] for ripping and tearing food apart, in contrast to the large, flat molar tooth for chewing and grinding food.

3.2. Gradient

Functional gradients and heterogeneities in the chemical composition and structural characteristics, involving the arrangement, distribution, dimension and orientation of building units, as well as graded interfaces, are generally adopted by natural materials to combine mechanical superiorities from different constituents and positions.[173,174] More specifically, the capabilities of natural weapons to attack and defense are usually strengthened at differing positions and combined through gradients.

3.3. Hierarchy

Through complex biologically controlled self-assembly processes during growth, structural regulation is performed in natural materials in a remarkably precise manner at a range of lengthscales, e.g., from nano- to macrolevels, as represented by the shark tooth,[90–92] leading to intricate multiscale architectures.[55,56] This is critical for Nature's weapons to perform appropriately as the mechanical properties required for attack and defense may originate at differing dimensions.

3.4. Self-Adaptive/Self-Healing

The restoration of the performance of natural weapons, following damage during use, is accomplished by autonomic self-adaptation and self-healing behavior. A case in point is the self-sharpening of teeth and tooth-like structures and the self-recovery of organic-containing materials under hydrated conditions which are tightly associated with the viscoelasticity of the organic phase.[108,118,182,183] Such a hydration response can be extremely effective. A case in point is with hypermineralized weapons, where an indentation crater formed in tooth enamel can be mitigated (by up to 32% in depth) within 100 min, despite the fact that enamel possesses only minimal organic content (≈1 wt.%).[43,186]

3.5. Support System

In a systematic framework, the functions of natural weapons are aided by various instruments that act to either amplify the attacking efficiency or minimize possible self-damage. The former is represented by the mantis shrimp saddle which serves to store and release a large amount of elastic energy for a swift strike of the raptorial foreleg;[126] while the hyoid apparatus of woodpecker is a good example of the latter that helps absorb impact energy and alleviate stress waves during pecking to protect the bird's brain from injury.[26,187–189]

3.6. Multifunctionality

The material systems that play a major role as weapons are often used for other aspects besides simply their mechanical attributes, such as communication, thermoregulation, camouflage, and courtship display—this is exemplified by the billing behavior of birds using their beaks.[190] Such multifunctionality suggests an integration of structural and functional properties implicit in Nature's design of materials.

3.7. Differences from Nonweaponized Materials

As compared to nonweaponized biological materials, the natural weapons are often subject to more stringent applications, especially for operating attacks. This necessitates remarkably superior mechanical properties and leads to the evolution of a series of intricate, and sometimes costly, designs that are unique to weapons. Chemical components that are uncommon to other materials may be adopted. Examples include the magnetite minerals in the chiton radular tooth for abrasion resistance, and the fluoridation of apatite in the weapons of aquatic animals in order to decrease their solubility in water.[90–94,106,125] Additionally, the pursuit of a high attacking efficiency usually results in a protruding, sharpened geometry of the weapons to focus their power. Example are the barbs that are frequently developed in spear- or needle-like structures, e.g., stinger and spine.[141,143,149] This contrasts to the smooth, flattened form of many other materials, especially the armors, which acts to promote load redistribution and to mitigate stress concentration. Additionally, the surface region is often stiffened and hardened, e.g., by utilizing higher degrees of mineralization, to gain efficient load transfer to the opponents. A common approach to achieve this is to align the highly anisotropic structural elements towards the surface. Such design differs from the common motif of nonweaponized materials where the organization of constituents is frequently along a direction orthogonal to the external load.

Another feature that distinguishes natural weapons is that they are invariably graded materials. They utilize gradients, which sometimes are mechanically unnecessary in other materials, to develop offence towards one location and persistence towards another in order to combine these two essential properties. It is a fact that similar solutions have evolved between natural weapons and nonweaponized materials, e.g., both the piranha tooth and *Arapaimas* fish scale—a pair of rivals as weapon and armor—are featured by a hard exterior backed by a compliant interior.[31,32] However, the detailed chemical and structural designs, mechanics, and functions that they confer to organisms are markedly different between these materials. Additionally, many biological materials generate their protection and functional performance by sustaining notable plasticity or nonvital damage. Such mechanisms are usually beyond the tolerance of natural weapons as a sound physiological condition and structural integrity are essential to ensure their attacking capability.

4. Lessons from Natural Weapons: Biomimetics and Bioinspiration

Although a highly promising area of research, the adoption of such lessons from Nature with respect to naturally evolved weapons is still somewhat limited in providing new ideas in the face of current technical challenges. Indeed, in the entire spectrum of structural materials, realistically there are only but a few successful examples where such ideas have been implemented to solve real engineering problems oriented to commercial applications. Aside from a lack of understanding about the detailed means by which organisms produce their weapons, a major difficulty arises from the issues of biomimetically making these materials as the processing of synthetic materials and how materials are created in Nature are radically different. The "top-down" fabrication and subsequent engineering are common in the industrial production of large-scale materials yet usually demand stringent conditions and high energy input. This simply cannot be used to build multiscale material architectures with the same degree of organization as their biological counterparts where the processes of "bottom-up" growth and adaptation are exploited. Nevertheless, advances in materials processing technologies, especially the development of new methods such as 3D printing, magnetic-assisted processing, and the like,[66–74,191–200] have enabled fine structural control even down to the nanoscale. These processes are potentially making biomimetics more practical on an industrial scale by replicating several of the design principles of natural weapons. A good example of such state-of-the-art progress is a layered composite of carpet-like zinc oxide (ZnO) nanowires infiltrated with a polymeric matrix, mimicking many micro/nanostructural features of tooth enamel (Figure 7b).[199,200] The materials' synthesis starts with the hydrothermal growth of ZnO nanowires into a columnar architecture, followed by the filling of the internal space with a layer-by-layer deposition of polymers; such a process is repeated until a desired number of strata are attained. The enamel-like designs, e.g., the introduction of a viscoelastic organic phase, the ordered "vertical" orientation of the hard columns, and the nano/micrometer dimensions of all constituents endow the composite with previously inaccessible combinations of high stiffness and damping properties, coupled with lightweight, that are appealing for a range of applications.

Beyond guidance with regard to microstructures, the strategies extracted from natural weapons further present differing strategies for designing devices, tools and even infrastructures at much coarser lengthscales, thereby providing solutions to a broader range of technical problems. Such implementation of biological principles at the mesoscale to respond to a medical problem is exemplified by the invention of combined harpoon-like microneedles with toothed blades generated by ion etching which imitate mosquito's stylets, in aspects of form, shape, and size (Figure 7b).[102,201] By combining a central straight needle with two jagged outer ones, such a device generates enhanced capability, as compared to a single sharp-tipped needle, for easy insertion into a soft substrate from the cooperative motion between different parts, the saw-like cutting mode of the blades, and the reduced contact area with the substrate. This feature is highly favorable in clinical blood collection to minimize pain and bleeding. Another example of the translation of a natural geometric design to a synthetic macroscale tool is the notched stubble-cutting disc harrow used for plowing, which has been inspired by the paw of the mole—a claw that has largely evolved for digging (Figure 7b).[202,203] Smooth sickle-shaped blades, having a geometry resembling that of the polydactyl forepaws of moles, have been introduced into the disc. Such design is proved to be effective in alleviating the maximum stress exerted onto the disc surface and at the disc-stem junction while additionally reducing the draft force of the tractor during plowing.

The inspiration that can be gained from the natural weapons resides not only in the manner how they are made, e.g., the nano- to macroscale architectures of materials, but in the means by which they function. This is somewhat out of the scope of materials science and more associated with issues of mechanical engineering. Mimicking the operation or use of a biological material system may offer new possibilities for performance enhancement; indeed, the microneedles based on mosquito's stylets again are an illustrative example here.[201] Instead of directly puncturing the victim's skin, mosquitos vibrate their stylets, backward and forward, to cut the tissue of skin using the toothed blades. Such an operation remarkably lowers the penetration resistance and thus allows for a painless biting.[102,103] Similar strategy has been implemented, by applying microvibration, during the usage of bioinspired microneedles, thereby enabling their much easier insertion. Another instance where both the architecture and the working mode of natural weapons have been translated is a new type ground sampler based on the sea urchin jaws (mouthpart).[204] The sampling action is designed to replicate the opening and closing mechanisms of the Aristotle's lantern.

5. Perspective and Outlook

While many conventional approaches associated with materials' design and processing, such as the present trend in metal alloys of increasing compositional complexity, can often become overexploited, taking lessons from biological systems presents an enlightening strategy for the design of new materials with potentially unprecedented combinations of properties and/or functionality. The weapons developed during Nature's evolutionary arms race are an outstanding example in this respect. Nevertheless, the principles underlying many of Nature's solutions largely remain to be explored and integrated with the attributes of current artificial strategies, such as the large selection of synthetic components and cost-effective fabrication routes. In this context, the rapidly growing efforts in biological and bioinspired materials research need to be focused on answering two fundamental questions: why biological material systems are so effective in fulfilling their demands and how we can learn from this to solve technical problems in practice.

One major task associated with the first question is to expand the range of natural systems under study and to recognize the prime function that they have perfected though evolution. Special attention must be paid to discern the principal structural and mechanical designs that confer these functions, and to clarify the key details of their design (a prime example is the critical role of interfaces in dictating the mechanical properties of teeth[43,48]), in order to extract the underlying principles. Although beyond the reach of most current tools, a systematic analysis which allows for the integration of the micro-/nanocompositional and structural features, mesoscale organizations, and the macro geometries of natural materials, as well as their cooperation within any given system, is pivotal to fully unraveling the hidden wisdoms of Nature. In this respect, multiscale computational modeling studies are already playing a progressively important role by capturing the innumerable effects of hierarchical structures of both natural materials and their mimicked synthetic counterparts.[11,12,26,194,199] Besides their mechanical and functional superiority, what makes the research on biological systems potentially even more fascinating is their capability of self-adaptation and self-healing in response to the exterior and interior stimuli.[177–179,198] We have merely "scratched the surface" of trying to mimic these critical properties, which must remain a key focus of the bioinspired design of new smart materials and systems in the future.

The solution to the second question rests largely on our ability to enact effective control of the material's architectures at multiple lengthscales. This differs markedly from most current processing methods that can regulate structural features over no more than a few dimensions, e.g., the phase composition and grain size. Such multiple-scale structuring of materials, instead of simply adjusting their compositions, still remains a challenge, especially for the majority of engineering alloys and ceramics that necessitate extreme fabrication conditions. Nevertheless, early promise has been realized by the increasing robustness of new processing routes, including additive manufacturing, freeze-casting, and magnetic-directed self-assembly,[66–74,191–198] as well as the combination of several such techniques, such as freeze-casting followed by mineralization and the crystal growth along with layer-by-layer deposition technique, described above.[199,205] An additional challenge is to combine the mechanical properties of materials with desired functionalities, specifically the autoresponsive capability to environmental changes.[198] Equally important is to unify the design and forming processes of materials and components in a similar manner as the growth of organisms. Moreover, the replication of the means by which Nature uses its materials offers new possibilities to obtain enhanced performance in man-made systems. Finally, the use of biomimetics and bioinspiration should preferably be geared to meet specific technical demands with a clear expectation of performance to avoid the misuse of natural strategies. New materials, particularly those oriented for structural use, will generally have to be made in bulk form in an economical fashion so as to be reasonably competitive for practical applications where performance is not the sole or even major consideration.

The exploration of biological materials represents almost an unlimited task in view of Nature's endless biodiversity. However, fresh lessons can also be generated by re-examining already known systems, particularly with regard to the notion of convergent evolution in Nature. For instance, a novel design motif that the protective role of materials can be enhanced by creating site-specific properties via gradient structural orientations has recently been extracted from a series of literature-reported biological tissues and materials.[104] On the other hand, the concepts of biomimetics and bioinspiration are not so rigid as to be confined to replicating the complex naturally occurring architectures, but rather, it seeks to implement the underlying principles and the unification and cooperation of different components. Moreover, the advantages of the well-established materials processing techniques are too evident not to be abandoned for the implementation of natural strategies. We anticipate that suitable modifications of such approaches, besides the development of new methods, will be an effective means to integrate the benefits from both the biological and artificial worlds. The principle is to fully create processing routes that can remain large-scale, flexible, and economic yet still capture the fundamental essence of natural design.

To summarize, we conclude that aside from increasing our understanding of the basic science of Nature, the insights into biological material systems, as represented by the current topic of Nature's arms race, will undoubtedly provide further inspiration towards achieving enhanced material properties and functionality in man-made systems. Such an approach offers an increasing promise of innovative solutions to current and upcoming technical challenges involving the future development of materials with superior properties and performance.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bioinspiration, biological materials, gradients, hierarchical structures, mechanical properties

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