ZHENHAI XIA

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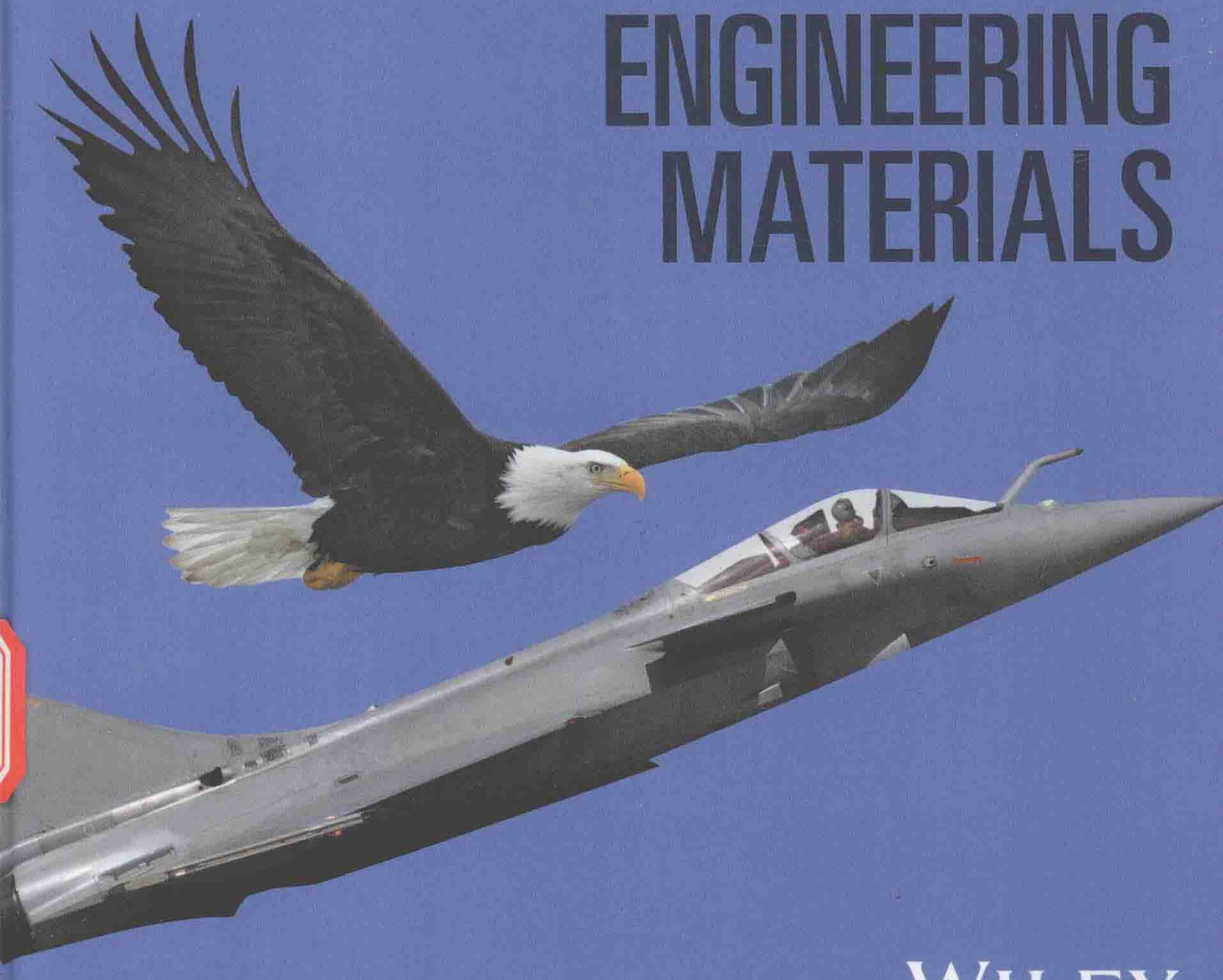

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Preface

Material designs by nature are quite different from traditional engineering concepts, and offer a vast reservoir of elegant solutions to engineering problems. Nature uses ingenious methods to create a large variety of materials with outstanding physical and mechanical properties. These materials are built at ambient temperature and pressure from a fairly limited selection of components. Thus, their extraordinary properties stem not from what or how they are made, but from their unique microstructures. Mimicking these biological materials designs and processes could create advanced engineering materials useful for various applications ranging from portable electronics to airplanes. However, natural designs of biological materials have proven difficult to mimic synthetically mainly because of a lack of knowledge of materials structure–property relationship and process methods. As a result, there is a growing requirement for the academic, research, and industrial communities to understand biomimetic materials design principles and look for innovative ways of addressing these issues.

This book explores novel biomimetic materials design concepts and materials structure–property relationships, as well as their implementation from a materials science and engineering perspective. It starts by understanding the microstructures of natural materials (e.g., squid beak, gecko footpad, butterfly wings, etc.) and then extracts biomimetic strategies on how to create advanced structural and functional materials though examining the microstructure relationship of these biological materials. These bioinspired design concepts and strategies, together with examples of how they are implemented, are then applied to synthetic materials. It is believed that considerable benefits can be gained by providing an integrated approach using bioinspiration with materials science and engineering.

This book was initiated when I attended the ASME conference as the session chair of the Bioinspired Materials and Structures Program in November 2012. I acknowledge that the topics covered in this book only scratch the surface of a considerable amount of both completed and ongoing research in a wide variety of disciplines. Yet, efforts have been made to provide fundamental understanding of the biomimetic principles and draw general viewpoints across the different topics. I hope this book will empower the reader to think beyond the current paradigms of biomimetic materials science and engineering when translating bioinspired design concepts to engineering reality.

I am indebted to a large number of colleagues for discussions and inputs that led to the writing of this book. I gratefully acknowledge my family, especially my wife, Shuqin Zhu, and my daughter, Serena Xia, for all their patience, help, and understanding while I completed this book.

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General Introduction

1.1 Historical Perspectives

Living organisms in nature have evolved over billions of years to produce a variety of unique materials that possess extraordinary abilities or characteristics, such as self-cleaning, self-healing, efficient energy conversion, brilliant structural colors, intelligence, and so on. These biological materials are made by nature using earth-abundant elements at ambient temperature, pressure, and neutral pH. Mimicking these biological materials structures and processing could lead to the development of a new class of advanced engineering materials useful for various applications ranging from transportation (e.g., aircraft and automobiles) to energy production (e.g., turbine blades, artificial photosynthesis), to biomedical products (e.g., implants, drug delivery). Some of these solutions provided by nature have inspired humans to achieve outstanding outcomes. For example, artificial dry adhesives mimicking gecko foot hairs have shown strong adhesion, 10 times higher than what a gecko can achieve,[1] and the strength and stiffness of the hexagonal honeycomb have led to its adoption for use in lightweight structures in airplane and other applications.[2]

The idea of mimicking nature's materials design has been around for thousands of years. Since the Chinese attempted to make artificial silk over 3000 years ago[2] there have been many examples of humans learning from nature to design new materials and related products. One of history's great inventors, Leonardo da Vinci, is well known for his studies of living forms and for his inventions, which were often based on ideas derived from nature.[3] Although the lessons learned by da Vinci and others were not always successful, as seen in the countless efforts throughout the ages by humans to fly like a bird, these explorations provided some clue for the Wright brothers, who designed a successful airplane after realizing that birds do not flap their wings continuously, rather they glide on air currents.[4] Perhaps the most common and successful product developed based on bioinspiration is Velcro, a fastener. In the 1940s a Swiss engineer, George de Mestral, noticed how

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the seeds of an Alpine plant called burdock stuck to his dog's fur. Under a microscope, he saw that the seeds had hundreds of tiny hooks that caught on the hairs. This unique biological material structure inspired him to invent the nylon-based fastener that is now commonly used.

Although the idea of learning from nature has been around for a long time, the science of biomimetics has gained popularity relatively recently. This approach, which uses nature's blueprints to design and fabricate materials, dates back to the 1950s, when the term "biomimetics" was first introduced by Schmitt in 1957.[5] Biomimetics is derived from *bios*, meaning life (Greek), and *mimesis*, meaning to imitate.[6] The term "bionics" was introduced by Steele[7] as "the science of systems, which has some function copied from nature, or which represents characteristics of natural systems or their analogues". The term "biomimicry", or imitation of nature, coined by Janine Benyus in 1997, refers to "copying or adaptation or derivation from biology".[8] From a materials science and engineering perspective, the science of biomimetic materials is thus the application of biological methods and principles found in nature to the study and design of engineering materials. This "new" science is based on the fundamentals of materials science and engineering, but takes ideas and concepts from nature and implements them in a field of technology. While the term "biomimetic" is frequently used in this book to describe mimicking the microstructure of biological materials, "bioinspired" is also employed to describe more general inspiration from nature.

The variety of life is huge; many things fascinate us. Leaves use sunlight, water, and carbon dioxide to produce fuel and oxygen. Geckos keep their sticky feet clean while running on dusty walls and ceilings. Some kinds of bacteria thrive in harmful environments by producing enzymes that break down toxic substances. Materials scientists are increasingly interested in how these phenomena work, and applying this knowledge to create new materials for clean energy conversion and storage, reusable self-cleaning adhesives, cleaning up pollution, and much more. Once the biomimicking succeeds, the impact is enormous.

1.2 Biomimetic Materials Science and Engineering

1.2.1 Biomimetic Materials from Biology to Engineering

Applying materials design principles taken from nature's design to engineering materials can create a new paradigm in materials science and engineering. The term "biomimetic materials science and engineering" is defined here as the study and imitation of nature's methods, mechanisms, and processes for the design and engineering of materials. Materials science, also commonly known as materials engineering, is a vibrant field creating various materials with specific properties and functions, and applying the materials to various areas of science and engineering. The knowledge, including physics and chemistry, is applied to the process, structure, properties, and performance of complex materials for technological applications. Many of the most pressing scientific problems that are currently faced today are due to the limitations of the materials that are currently available. As a result, breakthroughs in this field are likely to have a significant impact on the future of human technology. While humans make great efforts to look for better materials for technological applications, nature has already provided a vast reservoir of solutions to engineering problems, ready for us to exploit. Thus, it is necessary to extend materials science into biomimetic fields where scientists and engineers create materials with properties and performance beyond those of existing materials by mimicking nature-designed structures, and discover new routes for manufacturing materials

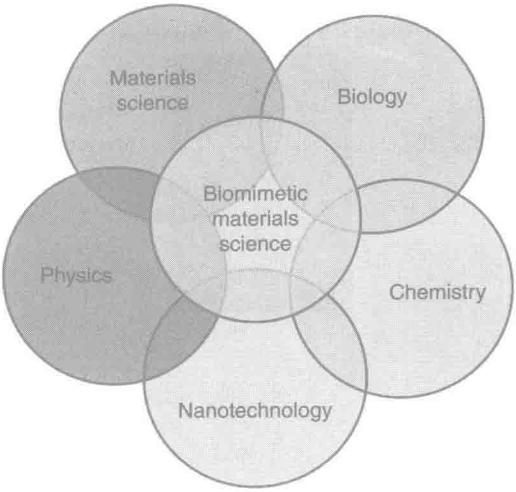

Figure 1.1 Scope of biomimetic materials science and engineering, and its relationship with other disciplines.

by imitating biological processes. The integration of biology, material sciences, chemistry, and physics together with nanotechnology and information technology has brought the subject of biomimetic materials to the science and engineering frontier (Figure 1.1); it represents a major international competitive sector of research for this new century.

1.2.2 Two Aspects of Biomimetic Materials Science and Engineering

Biomimetic materials science and engineering advocates looking at nature in new ways to fully appreciate and understand how it can be used to help solve problems related to materials design and processing. This is achieved by considering nature as model, measure, and mentor in two ways (Figure 1.2). The most obvious and common type of biomimetic materials is the emulation of natural material structures or functions. In this aspect, artificial materials that mimic both the structural form and function of natural materials are designed and fabricated using modern technology. With better understanding of the microstructure, chemistry, and function of biological systems, artificial materials with more precisely controlled microstructure and better function can be designed and produced by following biomimetic principles. With advances in nanotechnologies, biological materials can now be characterized at the level of atoms and molecules, and the biomimetic design of materials can be carried out on the same atomic and molecular scale. Computer modeling and simulations can further optimize the biomimetic design and even create new materials based on biological prototypes.

Emulating nature in the process is another aspect of the biomimetic design of engineering materials, which involves learning from the way nature produces things or evolves. Traditionally biomimetics has involved making artificial materials that replicate biological systems by conventional methods, but now it is possible to utilize biomolecules (nucleic acids, proteins, glycoproteins, etc.) and microbes (archaea, bacteria, fungi, protista, viruses, and symbionts) to actually fabricate artificial materials. This development has the potential to

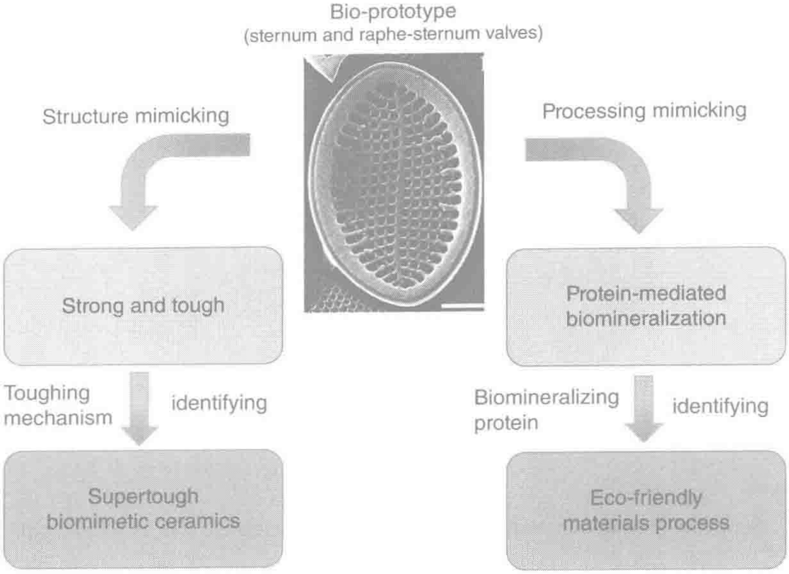

Figure 1.2 Two aspects of biomimetic materials science and engineering: structure and process mimicking. Image shows the structure of sternum and raphe-sternum valves of *Cocconeis scutellum* var. *scutellum* (scale 5 μm). Source: De Stefano *et al.* (2009).[9] Reproduced with permission of Elsevier.

revolutionize materials processing because biosystems synthesize inorganic materials like apatites, calcium carbonate, and silica with nanoscale dimensions.[3] Unlike the traditional materials processes that involve high temperature and high pressure with emission of toxic substances, biological systems produce materials under ecofriendly environments. Beyond the synthesis of nanomaterials, biological systems possess the ability to assemble nanoparticles into larger structures (e.g., bones and shells), effectively performing large-scale integration of nanoparticles. As opposed to the traditional engineering approach, biological materials are grown without final design specifications, using the recipes and recursive algorithms contained in their genetic code.[3] This provides new approaches for materials scientists and engineers to scale up nanoparticles into bulk materials or large structures with desired properties or functions, although this is more challenging than making nanoparticles. Mimicking these bio-assembly processes promises to be an enormously fruitful area of biomimetic manufacturing for advanced engineering materials.

1.2.3 Why Use Biomimetic Design of Advanced Engineering Materials?

Although tremendous progress has been made in the field of advanced materials beyond traditional materials, there still remain technological challenges, including the development of more sophisticated and specialized materials, as well as the impact of materials production on the environment. Many scientists and engineers, whether mechanical, civil, chemical, or electrical, will be looking for new and better designs involving materials. Over some 150 million years, nature has created and tested materials structures from nano and micro to macro and mega, using the principles of physics, chemistry, mechanics, materials science, and many other fields that we recognize as science and engineering. These materials, or "products", have been ruthlessly prototyped, market-tested, upgraded, refined, and otherwise improved as the world around them changed. Each of these fragile specimens is a package of innovation waiting to be understood and adapted as a biological prototype for advanced engineering materials. This evolution produced sophisticated materials and structures which rarely overlap with the methods and products made by humans.

In addition to new materials that could be fabricated based on biological design principles, biomimetic materials could be created that are better than the biological prototypes themselves in some aspects since the bioprototypes are optimized based on the elements available in their environments. Compared to nature, a multitude of synthetic materials with diverse properties are available for selection. Nature has achieved various functions or performances via microstructures restricted to limited kinds of biological materials, mainly collagen and minerals. In contrast, there are abundant artificial materials, including metals, ceramics, and polymers, with various properties facilitating the design and fabrication of microstructures. For example, artificial materials can provide refractive indexes of up to 2.0 and higher for building optical structures while most biomaterials are restricted to an index below 1.5.[10] Besides refractive index contrast, metamaterials with properties that do not exist in nature can be employed to create unique optical effects. To transfer the sophisticated design in nature, materials scientists need to design a broad range of fabrication approaches and adopt various artificial materials to fabricate microstructures with desirable features based on biological design principles.

Many biological materials have remarkable properties that cannot be achieved by conventional engineering methods, for example a spider can produce huge amounts (comparing with the linear size of his body) of silk fiber, which is stronger than steel, without access to high temperatures and pressures. Through biomimetics, it is possible to produce synthetic fibers with properties similar to those of natural fibers. These properties are achieved by mimicking the composite structure and hierarchical multiscale organization of the natural fibers.[11]

Biological materials are different from traditional engineering materials in a number of interrelated ways (Table 1.1). These differences may provide excellent opportunities for biomimetic materials science and engineering to create advanced engineering materials for various engineering applications. In terms of structures, the differences include the following:[12]

1. *Hierarchy.* Biological materials with different organized scale levels (nano to macro) exhibit distinct and translatable properties from one level to the next. A systematic and quantitative understanding of this hierarchy could provide a new route to building more complex synthetic materials with desirable properties and functions.
2. *Multi-functionality.* While many synthetic materials are designed for one function, most biological materials serve more than one purpose. For example, feathers provide flight capability, camouflage, and insulation, whereas the coating on moth eyes provides anti-reflection, self-cleaning, and protection functions.
3. *Self-healing capability.* Unlike synthetic materials in which damage and failure occur in an irreversible manner, biological materials often have the capability to heal damage or injury because of the vascular systems embedded in the structure.

Table 1.1 Comparison between biological materials, traditional engineering materials, and biomimetic materials (adapted from Fratzl (2007)[12]).

Materials	Biological materials	Engineering materials
Chemical compositions	Mostly earth-abundant elements: C, H, O, N, Ca, P, S, Si, etc.	Large variety of elements: Fe, Cr, Ni, Al, Si, C, N, O, etc.
Formation/ fabrication	Growth by genetically guided self-assembly (approximate design)	Fabrication from melts, powders, solutions, etc. (exact design)
Processing	Ambient temperature, pressure, neutral pH	Involve high temperature, high pressure, strong acid/base
Microstructure	Hierarchical structures at all length scales	Mostly microstructures at single length scale
Functions	Adaption of form and structure to the function, multifunctionality	Selection of materials according to function
Design criteria	Modeling and remodeling capability of adaption to changing environmental conditions	Secure design (consider large safety factor)
Failure prevention	Healing: capability of self-healing	Component replacement
Environmental impact	Biodegradable	Biodegradable/ non-biodegradable

4. *Evolution.* Biological structures are not necessarily optimized for all properties but are the result of an evolutionary process leading to satisfactory and robust solutions. "Living" materials (e.g., bone) have evolved in response to their environments during their lifetime.
5. *Environmental constraints.* Biological materials are limited in the elements they are composed of (e.g., C, H, O, N, Fe, etc.) and the availability of these elements dictates the morphology, properties, and functions of the materials.

The differences in processing between biological materials and traditional engineering materials could include the following:

1. *Self-assembly.* In contrast to many synthetic processes, most biosystems assemble structures from the bottom up, rather than from the top down.
2. *Mild synthesis conditions.* The majority of biological materials are synthesized at ambient temperature and pressure as well as in an aqueous environment, a notable difference from synthetic materials fabrication.
3. *Macromolecule-mediated processes.* Most biological processes involve macromolecules as templates, transporters, and catalysts for templating, guiding, and catalyzing the nucleation and growth of biomaterials, especially biominerals.

Biomimetic materials science and engineering also contribute to economy. Some examples found in nature that are of commercial interest include self-cleaning materials, drag reduction in fluid flow, energy conversion and conservation, high and reversible adhesion, materials and fibers with high mechanical strength, biological self-assembly, and antireflection. The applications of these biomimetic materials could generate an enormous market for new products. It is estimated that activity in the field of innovation based on nature increased