“十二五”国家重点图书

Advanced Functional Materials Series

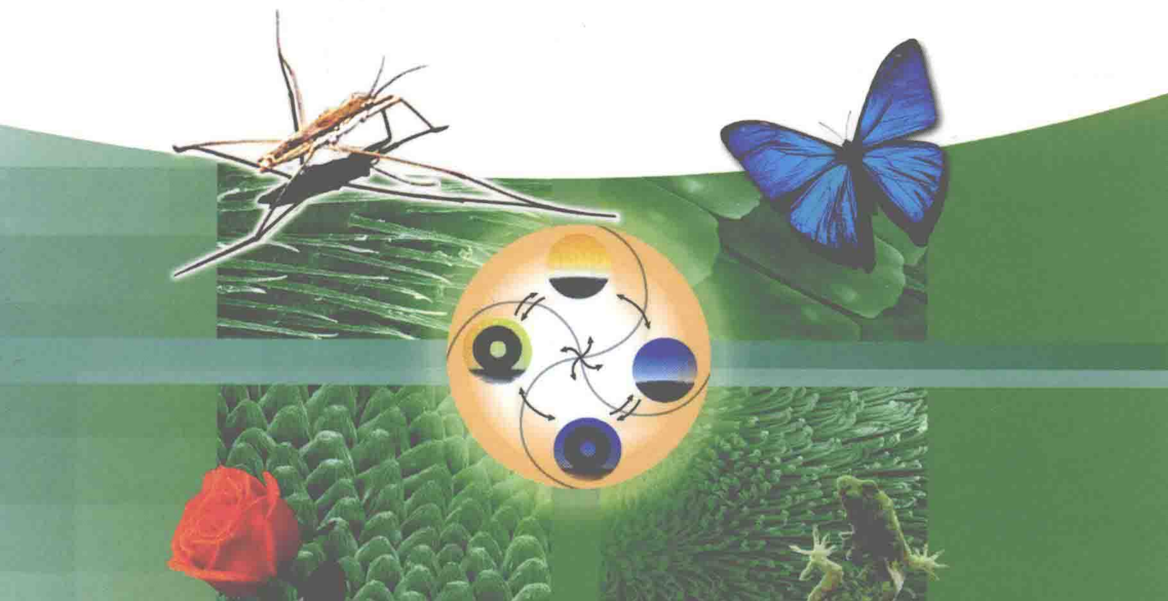
先进功能材料丛书　丛书主编　师昌绪

Bioinspired Intelligent Nanostructured Interfacial Materials

仿生智能纳米界面材料

Lei Jiang　Lin Feng

江　雷　冯　琳　著



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·北 京·

智能材料是20世纪90年代新兴的一种复合功能材料。智能材料体系，包括多级次结构与功能，是一个认识自然、模仿自然，进一步超越自然的研究过程。它也为科技的创新提供了新的思想，新的理论和前沿的方法。因此，模仿自然界生物的微纳米结构与功能将为生物与技术之前建起一座桥梁，这将为解决今天我们所面临的技术问题提供新的启示。

本书从智能材料入手，试图对仿生智能纳米界面材料进行尽可能的全面介绍，并重点讨论具有特殊浸润性的仿生智能纳米界面材料，第1章概述了智能材料的定义、仿生智能纳米界面材料的设计思想和典型实例及仿生纳米界面材料的智能化设计等。第2章介绍了几种自然界中具有特殊表面性能的生物体，如自清洁荷叶、在水面行走的水黾、在墙壁上行走的壁虎、沙漠集水的甲虫、具有特殊结构颜色的蛋白石、蝴蝶翅膀、孔雀羽毛等。第3章从理论上阐述了表面微结构与特殊宏观浸润性能之间的必然联系。第4章介绍了仿生超疏水表面，描述了几种典型的制备方法。第5章介绍了具有特殊浸润性的智能纳米界面材料。第6章为结论与展望。

本书对自然与人造微纳多尺度界面材料进行了一个较为全面的介绍，重点介绍了具有特殊浸润性的智能界面材料。受自然启发，作者提出一个“二元协同微纳米界面材料”的新概念。基于这种设计理念，异质材料的接触与耦合将为表面与界面材料带来全新的性质，这将创造出新的材料与器件。本书将科普与专业相结合，非常适合包括专业研究人员和科学爱好者。

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Preface

Intelligent materials are emerging composite materials that have boomed since 1990s. These novel materials have gained outstanding achievements and influenced multidisciplinary fields in recent years. In the 21st century, the content of intelligent materials is continuously expanding and the domains of which are constantly being broadened. The outstanding features are the tight connection between fundamental researches and practical applications, as well as the tight coupling of biomimic technology and nanotechnology. The intelligent material system is of great scientific significance; it combines studies that explore nature, mimic nature and surpass nature, involving a multitude of structures and functions. It provides new ideas, new theories, and new methodologies for the innovation of science and technology. After millions of years of evolution, plants and animals have completely and perfectly adapted to natural environments. Thus, mimicking the natural microstructures and functions of these creatures will build a bridge between biology and technology, which may provide inspirations for solving today's technological problems.

By summarizing the research findings on the synthesis, properties, and applications of photonic/electrical stimulative intelligent interfacial materials, the authors were the first to propose the concept of "Binary cooperative complementary micro/nanoscale interfacial materials". According to this design idea, the contact and coupling of heterogeneous materials will result in novel properties on the surface or interface of materials, which may create new functional materials and devices. For example, the investigations on superamphiphilic surfaces (the material's surface are both superhydrophilic and superoleophilic), superamphiphoblic surfaces (the material's surface are both superhydrophobic and superoleophobic), and smart switchable superhydrophobic/superhydrophilic materials will be of important applications in daily life, environmental protection and a good number of other domains.

This book devotes to give a complementary introduction about biomimic intelligent micro/nanoscale interfacial materials, paying attention to the intelligent materials with special wettabilities. The first chapter summarizes the definition of the intelligent materials, the design ideas and representative examples of biomimic intelligent micro/nanoscale interfacial materials. The second chapter introduces some natural creatures that possess special surface properties, including self-cleaning of lotus-leaf, walking-on-water of water strider, walking-on-wall of gecko, water-collection of desert beetle, special structural color of opal, wing of butterfly, feather of peacock and many others. In Chapter 3, we demonstrate the relationship between surface microstructures and special wettabilities in theory. The fourth chapter gives some typical manufacturing method of biomimic superhydrophobic surfaces; the fifth chapter introduces intelligent micro/nanoscale interfacial materials with special wettabilities. In the last and sixth chapter, we give conclusion of intelligent materials with some personal perspective in this area.

This text has tried to strike a balance between specialty and popular science. It has summarized a great deal of relative literature and the authors' research foundings on biomimic intelligent micro/nanoscale interfacial materials in recent years. It can be used not only as a reference book for researchers in areas including chemistry, material science and biology, but also for scientific enthusiasts. The authors would be very gratified if this book could spur readers' interests on biomimic intelligent micro/nanoscale interfacial materials.

This book is the collective effort and creative results of the research group led by the authors. It would not be possible without the help and support from many colleagues. The authors would like

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Chapter 1

Summary of Biomimetic Smart Nano-scale Interfacial Materials

In a sense, the progress of human society is based on the development of materials. Materials with excellent performance accelerate the development of human society; the development of society also desires more new materials. In the 21st century, the target of material sciences has changed from research on relationship between chemical composition, structure and performance of materials to the systemic investigation of the materials, including the fabrication and processing of the materials. It is characterized remarkably by the fact that material sciences and material technology have become very closely connected, while the core issue of the development of material science and technology is to discover and develop novel advanced materials. It has been a guiding concept in many research fields that novel materials and devices can be created by controlling the structures of materials and the peculiar functions of interface generated by contacting and amalgamating heterogeneous materials.

Smart materials are novel composite materials which have rapidly developed since 1990. They have attracted much attention for their wide applications and the evident influences on a variety of fields. For example, in modern medicine, smart material can be used to prepare artificial muscle, artificial skin, and drug delivery system; in military field, it can be used in the construction of warships to restrict the travel of noise, which is advantageous as it enhances the stealth performance of submarines and warships; in daily life, it can be used to enhance the performance and comfort of cars, and also used to change the color of houses at your pleasure. With the development of surface and interface sciences in mesoscopic scale, it is advantageous to the interaction of many significant subjects such as physics, chemistry, and material science, and also to the amalgamation of burgeoning sciences such as nanotechnology, biotechnology, and information science, though some new scientific theories are still needed to be established. In the 21st century, the connotation and fields of smart materials are enlarging gradually, the outstanding characteristic of which is the tight combination of basic research and applied research, biomimetic technology and nanotechnology. For instance, self-cleaning materials have been fabricated by mimicking microstructures and properties of lotus leaves; tires with more security have been produced by imitating the function of cat's forepaw pad combined with supple structure and properties of spider web; low-energy-loss airplane coating has been manufactured by mimicking the ribbed microstructure of the scales of a shark; and "smart glass" has been designed by imitating color changing mechanism of animals such as squid and others. Therefore, research on smart materials has attracted extensive interests in many fields, such as the design of structures and the new fabrication strategies.

1.1 Definition of Smart Materials

Smart materials refer to those special materials which are characterized by their intelligence as they can respond appropriately to stimuli from internal and external environment. Specifically, smart materials need to have properties as follows:

(1) can perceive, that is to detect and identify the intensity of stimuli from external (or internal) world, such as electricity, light, heat, stress, strain, chemistry, environment etc;
(2) can respond to external changes;
(3) can select and control the responses according to the designed ways;
(4) responses are sensitive, timely and appropriate;
(5) can return to the original state quickly when external stimuli are removed.

The concept of smart materials derives from bio-mimicking. It is to develop some new "live" materials with diverse functions similar to those of organisms. Therefore, smart materials must be able to perceive the stimuli, respond according to stimuli and control the responding behavior, which are three basic factors of smart materials. However, existing materials are usually too simple to meet the requirements of smart materials. Thus smart materials generally refer to smart material systems which are composite materials of two or even more kinds of materials. As a result, studies on the design, manufacturing, processing, property and structural characteristics of smart materials all involve the forelands of material sciences, which make smart materials the most active fields and the most advanced developing direction of material sciences, that will play an important role in world economy, society, national security, and the development of science and technology.

Stimuli-responsive smart materials possess perception, response and control functions when stimulated by external fields such as electricity, light, heat, stress, strain, chemistry, nuclear radiation etc. Studies on smart materials and development of smart devices have attracted closed attention of many scientists in the whole world. For example, Hu *et al.*[1] reported that the surface patterns on Poly(N-isopropylacryamine) hydrogel could be controlled and modulated by diverse environmental stimuli. Beebe *et al.*[2] introduced active hydrogel into microfluidic channels to act as valves, such that local flow inside microchannels could be controlled by using external stumili to adjust the expanded and contracted state of hydrogel. This result is very important in the transport of microfluid. Russell[3] reported a surface-responsive material, the response mechanisms and rates of which could be easily manipulated by changing the length, chemical composition, architecture, and topology of the polymer chains. Livage[4] summarized the stimuli-responsive materials — smart artificial muscles, and highlighted that the sheets made of entangled vanadium oxide nanofibers behaved like artificial muscles that contract reversibly on applying an electrical signal. Researchers from the Institute of Electron Physics, University of Stuttgart of Germany, invented a kind of smart solar clothes, which was a novel chemical fiber smart material using solar energy as energy resource, so that mobile telephone and electronic diary could be directly connected to the clothes.[5]

Biological smart interfacial materials are of great value in recognization and assembly of biomolecules and manipulation of complicated information. Kim and Abbott[6] reported that the specific binding of anti-biotin IgG to rubbed films of BSA functionalized by biotin could be detected by observing the optical appearances of liquid crystals supported onto these substrates. Liquid crystals were uniformly oriented when no antibody molecules were absorbed, while the alignment of liquid crystals was disrupted when complementary antibody molecules combined with antigens connected to BSA. Mason *et al.*[7] revealed that the excellent ability of identifying the sound sources of *Ormia* attributed to the special structures of its tympana(eardrums). Thereby, researchers prepared a tympana prototype which was suitable in ultrasonic range by using silicon to simulate the special tympana of *Ormia*. Furthermore, they invented a novel audiphone which could identify the direction of sound sources and enhance the effect of audiphones. This project had been recommended to the Ministry of Health and Department of Welfare of America as a demonstration project of results transforming by National Institutes of Health, USA in June, 2004.

Scientists from our country have done a lot of work with worldwide influence on fabrication, performances and theoretical studies of smart materials. Our group proposed a novel concept of "Binary Cooperative Complementary Interfacial Materials"[8] for the first time to guide the design and synthesis of new materials. We reported that the reversible transition between superhydrophobicity and superhydrophilicity on surfaces of nano-scale materials could be realized by stimulating with light, heat, etc.[9,10]

Professor Gu and co-workers from Southeast University of China has achieved great advances in studies on structural color and photonic crystals. Through thermo-processing method, they fabricated reverse opal photonic crystals by assembling composite nanospheres of polystyrene and silicon dioxide. Interestingly, the color of materials could be controlled conveniently by changing the structural periods.[11–13]

Professor Yang and co-workers from Jilin University of China reported that the colloidal crystals on PDMS stamp surface could serve as "ink" and be transferred onto the polymer-coated solid substrates by a modified microcontact-printing (μcp) technique. Polymer coatings were introduced to ensure effective interactions between colloidal crystals and substrates.[14–16]

Professor Yu and co-workers from the University of Science and Technology of China have done a lot of innovated studies on fabrication of biomimetic multi-scale structures. They fabricated many kinds of inorganic nano-scale materials by chemical synthesis combined with imitation of the process of biomineralization. They reported that helices of achiral inorganic nanocrystals could be fabricated in the presence of a racemic polymer at normal temperature and pressure, which provides theoretical and experimental basis to build inorganic materials with complex special structures.[17–20]

Academician Yao and co-workers from the Institute of Chemistry, Chinese Academy of Sciences (CAS) systematically studied novel optical functional materials from basic research to their applications, and have achieved a lot of innovative results.[21–24] They introduced the concept of supramolecular chemistry and molecular assembly technology into the design and building of inorganic photochromic materials for the first time, and photochromic ultra-thin films with nano-scale thickness which is much lower than the traditional micro-scale ones had been built. Moreover, the photochromic properties of these films could be regulated by changing the chemical micro-environments of building blocks, and the response time had been shortened from milliseconds to nanoseconds.

Liu *et al.* from the Center for National Nanosciences and Nanotechnology made important breakthrough in studies on building molecular devices by biological process. They built a pH-driven nucleic acid motor and explored its application, and the work provided theoretical and experimental basis to building novel artificial muscles.[25–27]

Professor Jiang and co-workers from the Institute of Chemistry of CAS found out that functionalized polydiacetylene vesicles could identify *Escherichia coli*, antibody-antigen, protein, etc. rapidly and easily as bionic cell identification devices, which may be further used to assemble bio-chips.[28,29]

Professor Chen and Prof. Xia from Nanjing University have done many groundbreaking works in the fields of nano-biological electrochemical analysis and microfluidic analysis system.[30,31] They used many chemical and physical means, such as supramolecular self-assembly, covalent bonding, electrochemical polymerization and adsorption, combined with methods of biology, physics and material sciences, to design and assemble a series of novel, reliable nano-scale molecular electronic devices with recognition properties. They also developed modern analysis methods and detection technology, established new principles in the detection of proteins and enzymes, as well as microfluidic analysis systems, and proposed a number of important biomolecular sensors.

1.2 Designing Concept of Bio-inspired Smart Interfacial Materials

The design concept of bionic smart interfacial materials has five levels: (i) Designing concept of biological intellectualization; (ii) Coordination of multi-scale structure effects; (iii) Design and synthesis of target smart stimuli-responsive molecules; (iv) Design of heterogeneous interfaces; and (v) Cooperative complimentary effect of weak interactions and bistable states.

1.2.1 *The bio-inspired concept*

Lives in nature have achieved all processes of intelligence through more than four billion years of evolution. Therefore, learning from nature should be the eternal theme for the development of smart materials.[32] Inspired by organisms in nature, we can mimic special functions of organisms from certain aspect to design smart materials, and we also combine the microscopic and macroscopic world. As a result, we may surpass the nature in some aspect eventually.[33]