

纳米材料的物理与化学

余大书
主编

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内容简介

纳米材料的物理与化学是关于在材料领域著名科学家在纳米科学与技术领域的归纳性总结，对纳米科学在材料的合成、结构、特性以及应用具有指导性意义。本书主要介绍了以下三个方面内容：纳米技术与科学基础；纳米科技的研究方法，例如理论、模型和仿真等；以纳米材料的合成和组装工艺为代表的纳米材料的研究方法；及纳米科学技术在物理、化学、生物以及新能源环境保护科学领域的广泛应用。

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Chapter 1

NANOSCIENCE AND NANOTECHNOLOGY FOR MATERIALS

1.1 VISION

Nanostructures are the entry into a new realm in physical and biological science. They are intermediate in size between molecular and microscopic (micron – size) structures. They contain a countable number of atoms, and are, as a result, uniquely suited for detailed atomic – level engineering. They are chameleons; viewed as molecules, they are so large that they provide access to realms of quantum behavior that are not otherwise accessible; viewed as materials, they are so small that they exhibit characteristics that are not observed in larger (even 0.1 μm) structures. They combine small size, complex organizational patterns, potential for very high packing densities and strong lateral interactions, and high ratios of surface area to volume.

Nanostructures are the natural home of engineered quantum effects. Microstructures have formed the basis for the technologies that support current microelectronics. Although microstructures are small on the scale of direct human experience, their physics is largely that of macroscopic systems. Nanostructures are fundamentally different; their characteristics—especially their electronic and magnetic characteristics—are often dominated by quantum behavior. They have the poten-

tial to be key components in information technology devices that have unprecedented functions. They can be fabricated in materials that are central to electronics, magnetics, and optics. Nanostructures are, in a sense, a unique state of matter—one with particular promise for new and potentially very useful products.

Because they are small, nanostructures can be packed very closely together. Their high packing density has the potential to bring higher speed to information processing and higher areal and volumetric capacity to information storage. Such dense packing also is the cause of complex electronic and magnetic interactions between adjacent (and sometimes, nonadjacent) structures. For many nanostructures, especially large organic molecules, the small energetic differences between their various possible configurations may be significantly shaped by those interactions. In some cases, the presence of surface interface material, with properties different from the nanostructures themselves, adds another level of complexity. These complexities are completely unexplored, and building technologies based on nanostructures will require in – depth understanding of the underlying fundamental science. These complexities also promise access to complex non – linear systems that may exhibit classes of behavior fundamentally different from those of both molecular and microscale structures.

Exploring the science of nanostructures has become, in just a few years, a new theme common to many established disciplines. In electronics, nanostructures represent the limiting extension of Moore's law and classical devices to small devices, and they represent the step into quantum devices and fundamentally new processor architectures. In molecular biology, nanostructures are the fundamental machines that drive the cell— histones and proteosomes—and they are components of the mitochondrion, the chloroplast, the ribosome, and the replication and transcription complexes. In catalysis, nanostructures are the tem-

plates and pores of zeolites and other vitally important structures. In materials science, the nanometer length scale is the largest one over which a crystal can be made essentially perfect. The ability to precisely control the arrangements of impurities and defects with respect to each other, and the ability to integrate perfect inorganic and organic nanostructures, holds forth the promise of a completely new generation of advanced composites. Each of these disciplines has evolved its own separate view of nanoscience; the opportunities for integrating these views and for sharing tools and techniques developed separately by each field are today among the most attractive in all of science.

Nanoscience is one of the unexplored frontiers of science. It offers one of the most exciting prospects for technological innovation. And if it lives up to its promise as a generator of technology, it will be at the center of fierce international competition.

1. 2 CURRENT SCIENTIFIC AND TECHNOLOGICAL ADVANCEMENTS

Nanoscience has exploded in the last decade, primarily as the result of the development of new tools that have made the characterization and manipulation of nanostructures practical, and also as a result of new methods for preparation of these structures.

Scaling Laws and Size – dependent Properties of Isolated Nanostructures

It is now well established that such fundamental properties as the melting temperature of a metal, the remanence of a magnet, and the band gap of a semiconductor depend strongly upon the size of the component crystals, provided they are in the nanometer regime. Almost any property in a solid is associated with a particular length scale, and below this length, the property will vary. For instance, the exciton diameter in a semiconductor may be tens or hundreds of nanometers, the distance between domain walls in a magnet may be hundreds of nanom-

eters, etc. This opens the prospect for creating a new generation of advanced materials with designed properties, not just by changing the chemical composition of the components, as has been done in the past, but by controlling the size and shape of the components. This creates great opportunities for fundamental science in condensed matter physics, solid state chemistry, materials science, electrical engineering, biology, and other disciplines.

Tools for Characterization

Scanning probe microscopies have revolutionized characterization of nanostructures, and development of new variants of scanning probe devices continues apace. Older tools, especially electron microscopy, continue to play essential roles. In biological nanoscience, the combination of X – ray crystallography and NMR spectroscopy offers atomic resolution structural information about structures as complex as entire virus particles.

Fabrication and Synthesis

Tremendous advances are currently occurring in the synthesis and fabrication of isolated nanostructures. These activities range from colloidal synthesis of nanocrystals to the growth of epitaxial quantum dots by strained layer growth. Related activities include the preparation of fullerenes, buckytubes, and other one – dimensional nanostructures, as well as the growth of mesoporous inorganics. Increased activity in the nanoscale design of polymers is also occurring, including the development of dendrimers and complex block copolymers. The techniques of molecular biology have made a very wide range of biological nanostructures readily available through cloning and overexpression in bacterial production systems.

While much has been accomplished in the growth of isolated nanostructures, work has only just begun in the use of self – assembly techniques to prepare complex and designed spatial arrangements of nano-

structures. A parallel line of current activity in fabrication of patterned nanostructures rests on the extension of techniques highly developed in the field of microelectronics: photolithography, X – ray lithography, and e – beam lithography. A number of recent developments in synthesis and fabrication offer the potential both to generate new types of structures, and, probably more importantly, to generate these structures at a fraction of the cost of techniques derived from microlithography. Soft lithography, which uses molding, printing, and embossing to form patterned structures in plastics and glasses, has expanded the range of materials that can be used and has suggested routes to previously inaccessible three – dimensional structures.

Computation

Because nanostructures contain few atoms (at least relative to most materials), they are uniquely susceptible to high – level simulation using supercomputers. The capability to treat nanostructures with useful accuracy using computation and simulation will be invaluable both in fundamental science and in applied technologies.

Emerging Uses

Many clear applications for nanotools and nanostructures are already evident and are the targets of existing technology development programs:

Giant magnetoresistance (GMR) materials have been introduced into commercial use with remarkable speed, and their acceptance suggests the importance of magnetic materials with nanometer – scale spin – flip mean free path of electrons.

Numerous nanodevices and nanosystems for sequencing single molecules of DNA have been proposed; these structures, if successful, will be invaluable in the Human Genome Project and other large – scale genomics programs. Indeed, it seems quite likely that there will be numerous applications of inorganic nanostructures in biology and medi-

cine, as markers.

Similarly, there exists a range of ideas for high – density information storage, based, for example, on concepts such as nano – CDs and on nanostructured magnetic materials, including materials showing giant and tunneling magnetoresistive effects; these promise to provide future systems for memory with ultrahigh densities.

New types of components for information processors based on quantum mechanical principles (resonant tunneling transistors; single electron transistors; cellular automata based on quantum dots) are being explored actively at the level of research; these types of processors appear to fit well in the burgeoning field of quantum computation.

New protective coatings, thin layers for optical filtering and thermal barriers, nanostructured polymers, and catalysts are already coming to the market.

Nanostructured coatings are showing good corrosion/erosion resistance as possible replacements for the environmentally troublesome chromium – based coatings.

Aerogels—highly porous, sponge – like materials with a three – dimensional filigree of nanostructures—have promise in catalysis and energy applications.

1.3 GOALS FOR THE NEXT 5 ~ 10 YEARS: BARRIERS AND SOLUTIONS

Numerous important areas require active research and development. The objectives of current research are to be able to understand the properties of isolated nanostructures; to make arbitrary structures with atomic – level precision; to do so rapidly, in large numbers, and inexpensively; and to design these structures to have desired properties using appropriate computer tools. Nanoscience is far from this objective, but it is moving rapidly in every component of the problem.

Fundamental Properties of Isolated Individual Nano-

structures

Individual nanostructures in isolation are the building blocks of nanotechnology. Individual structures are studied because we do not yet know the fundamental limits to the preparation of identical nanostructures and because each nanostructure can interact differently with its environment. Underlying the fundamental properties of nanostructures are two broad themes. First, the size – dependent properties of materials in the nanoscale regime are predicted to vary qualitatively according to scaling laws; comparison to these simple scaling laws remains an important activity. Second, the properties of isolated nanostructures have a significant statistical variation, fluctuating in time, and it is important to observe and understand these variations.

Many key questions relate to the structure, or arrangement of atoms, in a nanostructure. The relative stability of different structural phases is altered in the nanometer regime, affected by both kinetic and thermodynamic factors. Variations may arise for many reasons, including surface energies, absence of defects, or electronic quantum size effects. There is a compelling need to map out the kinetics and thermodynamics of phase transformations in nanostructures. For any picture of the physical properties of nanostructures to be complete, the structure of the surface must also be determined. Due to their finite sizes, the structure and composition of the surfaces of nanostructures may have particular importance for their chemical and physical properties. The surfaces of nanostructures are likely to vary significantly from the well – known structures of bulk surfaces, and entirely new experimental techniques for measuring these reconstructions. need to be developed. The ability not only to measure, but ultimately to systematically control, the surface and interior structures of nanoscale materials will be an ongoing field of research over the next decade.

Recent developments have permitted the observation of optical, e-

lectrical, magnetic, chemical, thermal, mechanical and biological properties of isolated, individual nanostructures. These techniques, which have facilitated developments such as single electron transistors, scanning probe microscopies, and single – molecule spectroscopy,

have revolutionized our understanding of nanostructured materials. The early studies point the way to a long – term agenda: develop new probes of fundamental properties that can work with nanometer spatial resolution and ever – improved temporal resolution and sensitivity.

Early work also reveals that nanoscale systems can be fluctuational by nature. Much work is needed to understand their fluctuations and to learn what the fundamental limits are. As an example, an important question in quantum computation concerns whether it is possible to prepare well – defined superposition of quantum states in nanostructures without rapid dephasing.

Fundamental Properties of Ensembles of Isolated Nanostructures

Nanostructures may be used in a wide range of contexts; most of these are ones in which ensembles of nanostructures are assembled into a complex, functional arrangement. Many properties of nanoscale building blocks vitally depend upon the size, the shape, and indeed the precise arrangement of all the atoms within. Thus, a high priority must be placed upon understanding the fundamental limits to the preparation of identical nanostructures. To this day, the processes of nucleation and growth are incompletely understood, and we do not know what is the largest number of atoms that can be assembled into a precisely defined molecular structure. Even if a system is prepared according to an ideal chemical process, there inevitably will be variations. There is a need to understand further which desirable properties are retained or even simplified by averaging out such variations, and which properties are lost.

Assemblies of Nanoscale Building Blocks

The construction of functional assemblies of nanostructures depends upon a sound understanding of the intrinsic couplings between nanostructures. Charge separation and transport, tunneling, through-space electromagnetic coupling, and mechanical and chemical interactions between nanostructures need to be measured and theoretically described further than has been done to date.

A combination of electron beam (and perhaps X-ray) lithography, scanning probe writing and fabrication, soft lithography, self-assembly, and catalytic growth together offer a rich menu of new and old fabrication techniques to use in patterning nanostructures. With the exception of e-beam and X-ray lithography, these techniques are all early in their development cycle and have substantial promise for growth. The next decade will see these techniques developed and integrated into a suite of methods for the fabrication of nanostructures and nanosystems.

The synthesis of bulk materials—colloids, magnetic structures, zeolites, buckytubes and analogs, aerogels, and many others—is also an area where there is potential for great innovation. In most of these materials, the physics underlying their behavior is understood only incompletely; there is an opportunity now to discover many new behaviors resulting from confinement of electrons or photons, from high structural perfection, from high ratios of surface to volume, or from some other aspect of small size.

In relevant but independent research in molecular biology, techniques of genetic manipulation, combined with technologies for protein production, provide the way to make small quantities of almost any protein of interest. The genome projects will extend this capability. Progress in biotechnology will increase the ease with which large quantities of genetic materials can be generated.

A key issue is understanding the integration processes of various isolated nanostructures and assemblies of nanostructures.

Evaluation of Concepts for Devices and Systems

Among the most critical impediments to thinking seriously about nanostructure—based systems are the difficulties in understanding how they are to be interconnected and addressed and in understanding what kinds of new functions are achievable. For instance, in nanoelectronics, there are a number of solutions that have been suggested for some of these issues—ranging from using buckytubes as nanowires to addressing individual components via ganged scanning probe devices, or even optically—but there has been almost no serious work directed toward the problems of systems fabrication.

Among the numerous questions that must be solved are: what to use as wires; how to design and fabricate devices; and what the architectures of systems should be.

Research is currently focused on exploring the fabrication and characterization of single devices at the level of single electron transistors or resonant tunneling devices. There is much less effort (and certainly much less than is needed) devoted to asking fundamental questions about how electrical current is to be carried from a contact pad to a device in a densely packed array, fault – and defect – tolerant designs, device isolation, the operation of large arrays of cooperative devices, and other fundamental questions dealing with the problem of making an array of nanostructured quantum devices that performs some complex function. Similar to the nanoelectronics issues, resolving the aspects related to integration at nanoscale is essential in dispersions, nanocomposites, sensors, and other areas.

Nanomanufacturing

Developing techniques for fabricating nanostructures inexpensively in very large numbers—that is, manufacturing them—is an area that

requires substantial effort; nanoscience will not be fully successful until it has provided the base for manufacturing technologies that are economically viable. It is probable that methods developed for microfabrication in the >100 nm size range will not work in the 20 nm range. It will thus probably be necessary to develop an entire new suite of manufacturing methods for nanostructures. There is reason to believe that self – assembly and soft lithography will be able to make substantial contributions to this important problem, but other fundamentally new methods will also be needed.

Connecting Nanoscience and Biology

One of the opportunities in basic science is to search for synergies between nanoscience in biology and nanoscience as developed in the contexts of computation and information science and solid – state physics and chemistry. There is no question that understanding the structure and function of biological nanostructures will stimulate fabrication of nonbiological materials; it is possible that biologically derived structures may also be useful in assembly of systems of nanodevices. In return, nanofabrication can provide analytical tools for investigating biomolecules (in genomics, proteomics, and high through put screening for drug leads) as well as for exploring the interior structure and function of cells. One objective of nanoscience should be to build robust intellectual bridges between its currently scattered disciplinary components, but especially between nanoelectronics and molecular biology.

Molecular Electronics

Molecular electronics offers an attractive opportunity for basic science in nanosystems. Organic molecules are probably the smallest systems that can be imagined for many possible functions, but they have the disadvantage, from the point of view of possible use in nanoelectronic systems, that they are usually poor conductors of electricity. A number of systems have been investigated in which experimental results