



高等学校“十二五”规划教材

Fundamentals of Nanomaterials

纳米材料基础

(双语版) (bilingual version)

张耀君 等编著



化学工业出版社



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张耀君 王亚超 刘礼才 编著
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· 北 京 ·

作为纳米材料的基础教材,本书以双语形式系统介绍了纳米材料的基本概念及分类,纳米效应,纳米材料的特性,“自上而下”和“自下而上”的纳米材料的制备方法,纳米材料的自组装,纳米材料的表征,碳纳米材料的制备,纳米制造中的光刻技术,纳米技术用于新能源研究等。本书简明扼要,内容新颖,知识系统,反映了纳米材料的基本内容和最新研究进展,有利于读者对纳米材料新知识的学习、拓展及延伸。为了便于学习,每章内容后都附有复习题、英文词汇和相应的译文。

本书可作为普通高等学校材料类、应用化学、化工、纺织、制药、环境、电子等专业的本科生及研究生教材,亦可供相关专业工程技术、科研人员参考。

图书在版编目 (CIP) 数据

纳米材料基础(双语版)/张耀君,王亚超,刘礼才
编著. —北京:化学工业出版社,2011.1
高等学校“十二五”规划教材
ISBN 978-7-122-10129-7

I. 纳… II. ①张… ②王… ③刘… III. 纳米材料-
双语教学-高等学校-教材-汉、英 IV. TB383

中国版本图书馆 CIP 数据核字(2010)第 244781 号

责任编辑:宋林青
责任校对:蒋 宇

文字编辑:孙凤英
装帧设计:史利平

出版发行:化学工业出版社(北京市东城区青年湖南街 13 号 邮政编码 100011)
印 装:三河市延风印装厂
787mm×1092mm 1/16 印张 11 字数 278 千字 2011 年 3 月北京第 1 版第 1 次印刷

购书咨询:010-64518888(传真:010-64519686) 售后服务:010-64518899
网 址: <http://www.cip.com.cn>
凡购买本书,如有缺损质量问题,本社销售中心负责调换。

定 价: 25.00 元

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前言

作为纳米科技基石的尺度在 $1\sim 100\text{nm}$ 范围内的纳米材料,因其独特的纳米效应,近年来已成为全球高新科技炙手可热的研究领域之一。纳米材料是一门涉及知识面广的新的交叉学科,新概念、新理论、新技术及新方法层出不穷。纳米科技充满着原始创新的机遇与挑战,尤其是纳米科技正在将微制造推向纳制造与纳加工的前沿,各种产品正从微尺度向纳尺度悄然转变,新材料、新产品呼之欲出,这将对信息产业、能源、环境检测、生命科学、军事、材料的生产与加工带来一场革命性的变革。因此,了解纳米科技的发展动态,加强对纳米材料的基本概念和基础知识的学习,掌握纳米材料的特性、制备原理及研究方法就显得十分重要。

本书是在作者多年来为本科生及研究生开设的“纳米材料基础”双语教学讲义的基础上,进行不断的修改、补充及完善后撰写而成的。在编写过程中,作者查阅了大量的国内外相关的文献资料,阅读了诸多的教材及专著,结合本研究小组的科研成果,以纳米材料的基本概念、纳米效应、纳米材料制备、表征、纳米制造以及纳米技术在新能源中的应用为主线,力图条理清楚、结构严谨地将基本概念及基础知识奉献给读者。本书具有以下特色。

(1) 为了将纳米材料的基础知识学习与阅读外文资料及提升科研能力相融合,双语编著是本书的特色之一。

(2) 为适应初学者学习,本书由浅入深,循序渐进,着力强化教材的基础性和系统性。

(3) 本书内容新颖,简明扼要,知识系统,重点突出,在强化基础知识、基本理论的同时,注重纳米科技的研究进展及最新成果介绍,体现基本理论与研究实践相结合的特色。

(4) 为了使读者能对自己感兴趣的内容进一步自学,书中对重要的概念、图表、实例等引注了出处,便于查阅导读;另外,为了便于阅读及掌握章节中的重点内容,每章后附有词汇、复习题及相关章节的译文。

本书共八章,第1章主要介绍了纳米材料的基本概念及分类,纳米科技的研究进展及最新成果。第2章涉及纳米效应的相关概念。第3章是关于纳米材料的力学、热学、磁学、电学及光学性能。第4章重点介绍了“自上而下”和“自下而上”的纳米材料的制备方法以及纳米材料的自组装。第5章对纳米材料的表征及纳米制造的常用仪器——扫描隧道显微镜和原子力显微镜的基本原理及操作模式进行了简述。第6章是碳纳米材料的制备及纳米车的雏形。第7章涉及纳米制造的光刻技术。第8章主要论述纳米技术用于太阳能制氢的新能源研究。

在编写过程中,作者阅读了大量的相关文献资料,从中获得了许多前瞻性的珍贵信息,向本书中引用的文献作者表示深深的谢意。化学工业出版社对本书的出版提供了大力的支持,在此一并表示衷心的感谢。

鉴于作者水平有限,编写时间仓促,本书中、英文疏漏和不足之处在所难免,敬请同行和读者批评指正。

编著者

2010年10月于西安

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1. Introduction to nanoscale materials

1.1 Introduction to the nanoworld

The nanoscale material with at least one dimension in the nanometer range is a bridge between isolated atoms or small molecules and bulk materials. Therefore, it is referred to as mesoscopic scale materials. Nanoscale materials as foundation of nanoscience and nanotechnology have become one of the most popular research topics in recent years. The intense interests in nanotechnology and nanoscale materials have paid to several areas by the tremendous economical, technological, and scientific impact: ① with exponential growth of the capacity and speed of semiconducting chips, the key components which virtually enable all modern technology is rapidly approaching their limit of arts, this needs the coming out of new technology and new materials; ② novel nanoscale materials and devices hold great promise in energy, environmental, biomedical, and health sciences for more efficient use of energy sources, effective treatment of environmental hazards, rapid and accurate detection and diagnosis of human diseases; and ③ when a material is reduced to the dimension of nanometer, its properties can be drastically different from those of the bulk material that we can either see or touch even though the composition is essentially the same. Therefore, nanoscale materials prove to be a very fertile ground for great scientific discoveries and explorations.

It has been said that a nanometer is “a magical point on the length scale”, for this is the point where the smallest man-made devices meet the atoms and molecules of the natural world ^[1].

Indeed, nanoscience and technology have been an explosive growth in the last few years. “Nanotechnology mania” is sweeping through essentially all fields of science and engineering, and the public is becoming aware of the quote of the chemist and Nobel laureate, Richard Smalley: “Just wait, the next century is going to be incredible. We are able to build things that work on the smallest possible length scales, atom by atom. These little nanothings will revolutionize our industries and our lives ^[1].”

1.2 Definition of nanoscale materials

1.2.1 Nanometer

The prefix “nano” is from the Greek word “nanos” and it means dwarf. Nanometer is a length unit. A nanometer (nm) equals a billionth of a meter ($1\text{nm} = 1 \times 10^{-9}\text{m}$).

Fig.1.1 shows the length scales of some materials synthesized and biology. Beginning at small scales, feature of Au atomic diameter is on the order of 0.1nm in size. The diameter of a carbon nanotube is about 1~2nm, and a double helix of DNA is about 3nm. A HIV virus is about 100nm

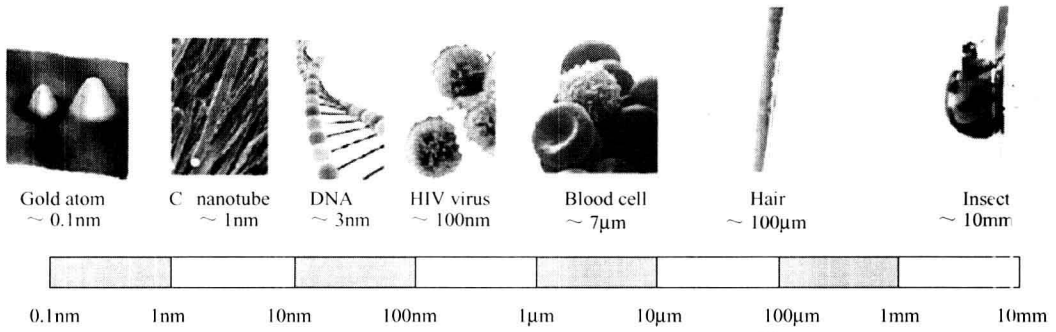


Fig.1.1 Length scale and some examples related ^[2]

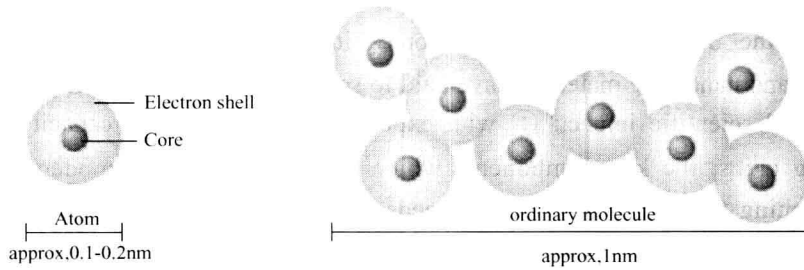


Fig.1.2 Schematic representation for atom and molecule

and so on ^[2]. The diameter of one atom is about $0.1\sim 0.2\text{nm}$, and the length of $8\sim 10$ atoms is about one nanometer as shown in Fig.1.2.

1.2.2 Definition of nanoscale materials

Nanoscale material is defined as a material having one or more external dimensions in the nanoscale ($1\sim 100\text{nm}$).

Fig.1.3 shows a picture of single-walled carbon nanotubes in comparison to a human hair which is about 80000nm in diameter. The single-walled carbon nanotube is about 1000 times smaller than that of human hair in diameter.

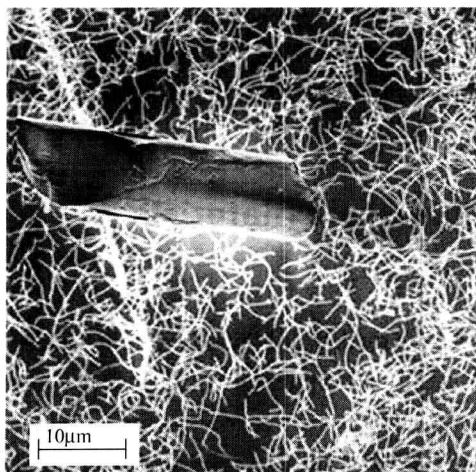


Fig.1.3 Human hair fragment and a network of single-walled carbon nanotubes

1.3 Classification of nanoscale materials

Nanoscale materials are primitively divided into discrete nanomaterials and nanostructured materials, but also there are other classification methods.

The discrete nanomaterial means that the material has an appearance characteristic at least one dimension on the nanoscale, such as nanoparticles, nanofibers, nanotubes and membrane.

The nanostructured material is the material has an appearance characteristic of bulk material, but it may be built up of discrete nanomaterials, such as bulk materials by consolidation nanopowders, or it may be composed of continuously nanostructural units, such as porous materials including microporous ($<2\text{nm}$), mesoporous ($2\sim 50\text{nm}$) and macroporous ($>50\text{nm}$), nanophase and polycrystalline materials.

The technique of consolidation nanopowders is a fabrication method of bulk nanostructured materials. However, because of the very small size of the powder particles, special precautions must be taken to reduce the interparticles friction and minimize the danger of explosion or fire. The powders themselves may have a microscale average particle size, or they may be true nanopowders, depending on their synthesis routes. They would be compacted at low or moderate temperature to produce a so-called green body with a density in excess of 90% of the theoretical maximum. Any residual porosity would be evenly distributed throughout the material and the pores would be fine in scale and have a narrow size distribution. Polycrystalline materials with grain sizes between 100nm and $1\mu\text{m}$ are made up of many nanocrystals and are conventionally called ultrafine grains.

1.3.1 According to the spatial dimension of materials

A reduction in the spatial dimension or confinement of nanoparticle in a particular crystallographic direction within a structure generally leads to changes in physical properties of the system in that direction. Hence one classification of nanostructured materials and systems essentially depends on the number of dimensions which lie within the nanometer range. The examples of reduced dimensionality systems are shown in Table 1.1 [3].

(1) Zero dimension (0D) materials There are three dimensions for material on the nanoscale. This means that the size of material is confined in three dimensions. This system includes the nanoparticles, nanocrystals and etc.

(2) One dimension (1D) materials There are two dimensions for material on the nanoscale. This means the size of material is confined in two dimensions. The system includes nanowires, nanorods, nanofilaments, nanotubes and etc.

(3) Two dimension (2D) materials There is one dimension on the nanoscale in material, that is, the size of material is confined in one dimension. The system includes ultrathin films, multilayered films, thin films, surface coatings, superlattices and etc.

1.3.2 According to the quantum properties of materials

(1) Bulk material The electronic structure of material is strongly related to the nature of material. We now consider the case of a three-dimensional solid in x -, y - and z - directions containing a number of “free” electrons. The “free” means those electrons are delocalized and not bound to individual atom.

Table 1.1 Examples of reduced-dimensionality systems

3D confinement
Fullerenes
Colloidal particles
Nanoporous silicon
Activated carbon
Nitride and carbide precipitates in high-strength low-alloy steels
Semiconductor particles in a glass matrix for non-linear optical components
Semiconductor quantum dots(self-assembled and colloidal)
Quasi-crystals
2D confinement
Carbon nanotubes and nanofilaments
Metal and magnetic nanowires
Oxide and carbide nanorods
Semiconductor quantum wires
1D confinement
Nanolaminated or compositionally modulated materials
Grain boundary films
Clay platelets
Semiconductor quantum wells and superlattices
Magnetic multilayers and spin valve structures
Langmuir-Blodgett films

For a bulk solid, the states are quasi-continuously distributed and the distance between two adjacent states is quite narrow. The energies are quasi-continuous and their density of states varies with the square root of the energy $E^{1/2}$ shown in Fig.1.4 ^[1].

(2) Quantum wells (2D) When a solid is fully extended along the x - and y -directions, but the thickness along the z -direction is only a few nm (see Fig.1.4), electrons can still move freely in the x - and y -directions. However, movement of electrons in the z -direction is restricted. Such a system is called two-dimensional (2D) system and is also named as quantum well.

The energy levels for the electron motion along the x - and the y -directions are quasi-continuous. The wavefunction Ψ_z at the border of a small “box” must be zero. This constraint causes discrete energy levels in the z -direction. Electrons can only occupy such discrete states ($n_z=1; n_z=2; n_z=3; \dots$). The position of energy levels changes with the thickness of the solid in the z -direction and the density of states shows “staircase”.

Quantum confinement naturally restricts the motion of the carriers in some ways. When the electronic motion is confined in one dimension (quantum confinement in one dimension) and the motion is free in the other two dimensions, it results in the creations of quantum wells or quantum films.

The quantum well implies that the electrons drop into a “potential well” as well as they are trapped in the film. 2D systems are usually formed at interfaces between different materials or in layered systems in which some of the layers may be only a few nanometers thick. Layers made by using different semiconductor materials may result in the trapping of carriers (electrons, holes) in a particular layer. The trapped carriers are restricted to movements in certain directions ^[4].

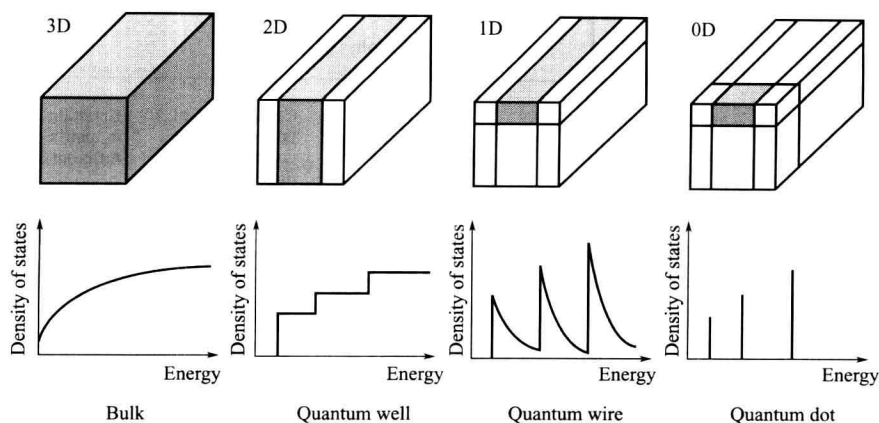


Fig.1.4 Electronic density of states for a bulk semiconductor (3D), quantum well (2D), quantum wire (1D) and quantum dot (0D) ^[1]

(3) Quantum wires (1D) Now electrons can only move freely in the x -direction, and their motions along the y - and z -axis are restricted by the borders of the solid. Such a system is called quantum wire. In one-dimensional systems, the electrons are free to move only in one direction with quantum confinement in the other two dimensions. The density of states along the x -axis is inversely proportional to $E^{-1/2}$ and thus exhibits singularities near the band edges. From each of the hyperbolas it is found that the energy band along the x -axis is quasi-continuous, but energies along the y - and z -axis are discrete shown in Fig.1.4.

(4) Quantum dots (0D) If the electrons are confined to a point in space, we get a zero-dimensional system, wherein the electrons are not free to move at all. Quantum dots with quantum confinement in three dimensions have discrete density of states, i.e. the electron energies are quantized in Fig.1.4. Quantum dots are also called artificial atoms or boxes of electrons, because of their discrete charge states and the energy-level structures which are similar to atomic systems containing from a few thousands to one electron ^[5].

1.3.3 According to material properties

The thousands of substances that are solids under normal temperature and pressure can be subdivided into metals, ceramics, semiconductors, composites, and polymers. These can be further subdivided into biomaterials, catalytic materials, coatings, glasses, and magnetic and electronic materials. All of these solid substances with their widely variable properties take on another subset of new properties when they were produced in the form of nanoparticles. They can be divided into different forms such as nanocrystal materials, nanoceramic materials, nanocomposite materials, nano high molecular materials and so on.

1.3.4 According to the shape and chemical composition

(1) Nanostructured materials According to chemical composition and dimensionality (shape) of the crystallites, the three categories of nanostructured materials (NsM), such as layer-shaped, rod-shaped and equiaxed crystallites, may be grouped into four families, that is, nanostructured materials are divided into 12 classes by Gleiter as shown in Fig.1.5 ^[6].

The boundary regions of the first and second family of NsM are indicated in black to emphasize the different atomic arrangements in the crystallites and in the boundaries. All crystallites and interfacial regions (black) have the same chemical composition in the first family.

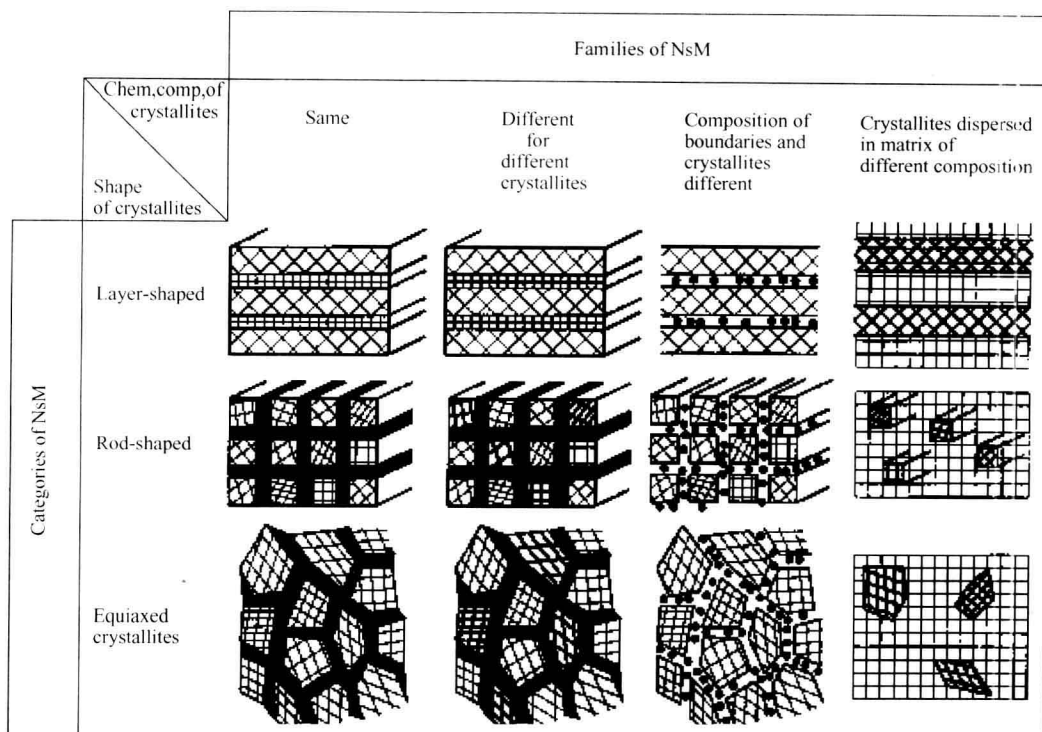


Fig.1.5 Classification schema for NsM according to their chemical compositions and the dimensionality (shape) of the crystallites (structural elements) the NsM [6]

In the second family, the boundaries (black) are the regions where two crystals of different chemical compositions are joined together causing a steep concentration gradient [6].

Some examples can be listed to understand NsM in detail. The semicrystalline polymers consist of crystalline lamellae separated by non-crystalline regions (first category in Fig.1.5) or NsM is made up of equiaxed nanometer-sized crystals, e.g. equiaxed crystals Cu (third category). NsM belonging to the second family is composed of crystallites with different chemical compositions (indicated in Fig.1.5 by different thickness of the lines used for hatching). Quantum well (multilayer film) structures are probably the most well known examples of this type (first category).

An interesting new type of material was recently produced by co-milling Al_2O_3 and Ga. It turned out that nanometer-sized Al_2O_3 crystals were separated by a network of non-crystalline layers of Ga. Depending on the Ga contents, the thickness of the Ga varies between less than a monolayer and up to about seven layers of Ga. The fourth family of NsM is formed by nanometer-sized crystallites (layers, rods or equiaxed crystallites) dispersed in a matrix of different chemical compositions. Precipitation-hardened alloys belong in this group of NsM. Nanometer-sized Ni_3Al precipitates dispersed in a Ni matrix generated by annealing a supersaturated Ni-Al solid solution are an example of such alloys.

(2) Nanostructures Nanostructures (NSs) should be separated from nanostructure materials (NSMs) because the former (NSs) are characterized by a form and dimensionality while the latter (NSMs) by a component in addition. Under a nanostructure we know the size d at least is less or equal to a critical value d^* , $d \leq d^*$ at nm scale. The value of d^* does not have a certain meaning because it is dictated by a critical characteristic of some physical phenomena (free path length of electrons, length of de Broglie wave and etc.) giving rise to the size effects [7].

According to dimensionality, NSs may be one of the fourth, 0D, 1D, 2D and 3D. All NSs can

be built from elementary units (building block) having low dimensionality 0D, 1D, and 2D. The 3D units are excluded because they can't be used to build low dimensional NSs except 3D matrix. However 3D structures can be considered as NSMs if they involve the 0D, 1D and 2D NSs. According to Pokropivny, the nanostructures (NSs) can be divided into 36 classes as shown in Fig.1.6 ^[7].

Dimensionality classification of nanostructures($L < 100 \sim 500\text{nm}$)

Designation: dimensionality of NSs $\rightarrow kD/mn.. \leftarrow$ dimensionality of elementary units
 $k \geq l, m, n \{k, l, m, n\} = \{0, 1, 2, 3\}$

Elementary building units :

1. 0D molecules, clusters, fullerenes, rings, metcarbs, thoroids, domens, particles, powders, grains, schwartzons	2. 1D nanotubes, fibers, filaments, whiskers, spirals, belts, springs, horns, columns, needles, pillars, helicoids, wires, ribbons	3. 2D layers
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0D-nanostructures :

4. 0D0 uniform particles arrays	5. 0D00 heterogeneous particles arrays, "core-shell" dendrimers, onions
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1D-nanostructures :

6. 1D0 molecular chains, polymers

7. 1D00 heteropolymers	8. 1D1 bundles, ropes, cables, corals	9. 1D11 heterochains, heterocables, saws, hair, heterobundles, junctions, combs, bows	10. 1D10 beads, pea-pods, fullereno-fibers
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2D-nanostructures :

11. 2D0 fullerene films	12. 2D1 nanostraw, PhC, fibers films
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13. 2D2 tiling, mosaic, layered films	14. 2D00 heterofilms of heteroparticles, fullereno-powders	15. 2D10 films of pods, fullereno-fibers	16. 2D11 films of fibers and nanotubes, PhC-waveguides
17. 2D20 fullereno-plate films	18. 2D21 bridges, fiber-layer films	19. 2D22 hetero-layers, MOS-structures	20. 2D210 fullerene-fiber-layer films

3D-nanostructures :

21. 3D0 fullerenes, clathrates, powder skeletons, fog	22. 3D1 skeletons of fibers, nanotubes	23. 3D2 layer skeletons, buildings, honeycombs, foams	24. 3D00 sols, colloids, smogs, heteroparticles composites
25. 3D10 skeletons of fibers-powders	26. 3D11 skeletons of heterofibers, nanotubes	27. 3D20 intercalates, skeletons of layers and powders	28. 3D21 cross-bar-layers, layer-fiber skeletons
29. 3D22 heterolayers	30. 3D30 opals, dispersions, particles, pores, fullerenes in matrix	31. 3D31 membranes, PhC, fiber composites, waveguides	32. 3D32 friction pairs, contacts, interfaces, cavities, grain boundaries
33. 3D210 composites of layers, fibers and particles in matrix	34. 3D310 membranes + impurities, powder-fiber composites	35. 3D320 powder-layers composites	36. 3D321 layers-fibers-composites in matrix, VCSEL

Fig. 1.6 Dimensionality classification of nanostructures ^[7]

Notices:

1. Interfaces between building units not regarded as additional 2D-NSs;
2. Inverse NSs with cavity building units not regarded as separate ones;
3. The classification may be extended with account of fourfold combinations

(3) **Nanocomposites** Nanocomposite refers to composites of more than one solid phase where at least one dimension is in the nanometer range and typically all solid phases are in the range of 1~100nm. The solid phases can be amorphous, semicrystalline, or crystalline, or combinations thereof.

The metal-ceramic and ceramic-ceramic nanocomposites can be divided into four categories: intergranular, intragranular, hybrid, and nano/nano composites^[8], intergranular nanocomposites, in which the nanoparticles are distributed at the grain boundaries of the ceramic matrix in Fig.1.7(a), intragranular nanocomposites, in which the metallic nanoparticles are dispersed inside grains of the ceramic matrix in Fig.1.7(b), hybrid composites, i.e. intra-inter composites, are shown in Fig.1.7(c), The nano/nano composites consist of two phases with grain sizes not more than 100nm in Fig.1.7(d).

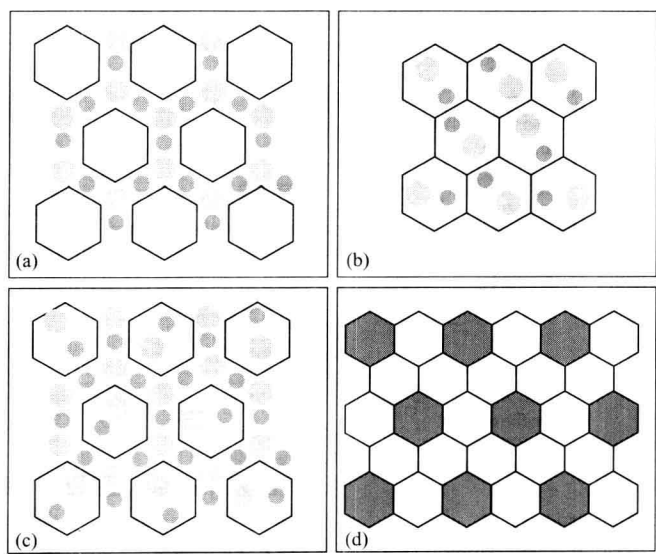


Fig.1.7 Classification of nanocomposites: (a) inter-type; (b) intra-type; (c) hybrid-type; (d) nano/nano-type^[8]

However, the number of classes can be reduced to just two. Indeed, there are no pure intragranular nanocomposites, because in any real material, there always is a certain proportion of metal particles at the surface, so that it is actually in the hybrid intra-inter class. The nano-nano composites must also be considered as a special case of the intergranular class^[9].

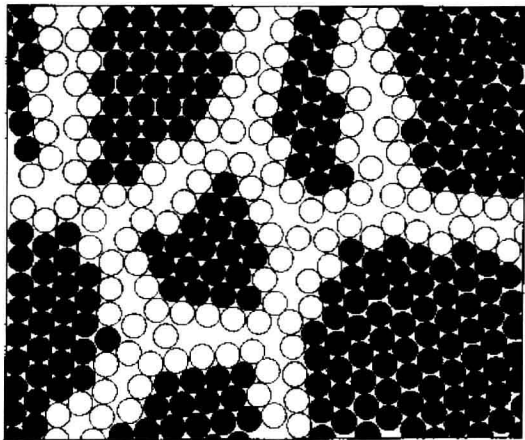


Fig.1.8 Schematic representation of a nanocrystalline structure on atomic scale^[10]

On atomic scale, if atoms are represented by circles (Fig.1.8), a two-dimensional representation of nanocrystalline structures can be considered as a mixture of two structural components. Nanograins with a crystal lattice of ordered atoms are denoted by black circles, and intercrystallite boundaries

are depicted with white circles in Fig.1.8. The average grain size of the nanocrystalline varies from 2nm to 100nm and can contain from 10^2 to 10^8 atoms. This nanocrystalline structures belong to nanocomposites^[10].

1.4 Nanoscale science and technology

Generally, nanoscience is the world of atoms, molecules, macromolecules, quantum dots, and macromolecular assemblies, and is dominated by surface effects such as Van der Waals force attraction, hydrogen bonding, electronic charge, ionic bonding, covalent bonding, hydrophobicity, hydrophilicity, and quantum mechanical tunneling.

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular, macromolecular scales where properties significantly differ from those at a larger scale^[11, 12].

Nanotechnology is the design, characterization, production, and application of structures, devices, and systems by controlling shape and size at the nanometer scale^[11, 12].

The term “nanotechnology” was first introduced by a Japanese engineer, Norio Taniguchi^[13]. The term originally implied a new technology that went beyond controlling materials and engineering on the micrometer scale, which had dominated the twentieth century.

Generally, nanotechnology should really be called “nanotechnologies”: There is no single field of nanotechnology. The term broadly refers to the fields such as biology, physics, chemistry, any other scientific fields, and also deals with controlled manufacturing of nanostructures.

In some senses, nanoscience and nanotechnologies are not new. Chemists have been making polymers which are large molecules made up of nanoscale subunits, for many decades and nanotechnologies have been used to create the tiny features on computer chips for the past 20 years. However, advances in the tools that now allow atoms and molecules to be examined and probed with great precision have enabled the expansion and development of nanoscience and nanotechnologies.

1.5 Driven by industrial revolution

In the field of electronics, for example, since the invention of the transistor by Shockley, Brattain, and Bardeen in 1940s, downsizing of the electronic devices has been continued.

Technology development and industrial competition have been driving the semiconductor industry to produce smaller, faster, and more powerful logic devices. In 1965, Gordon Moore, the cofounder of Intel Co., observed that the number of transistors per square inch on integrated circuits doubled every year since the integrated circuit was invented. Moore predicted that this trend would continue in the future. In the subsequent years, this pace slowed down, but the data density doubled approximately every 18 months. This is the current definition of Moore’s Law. Most of experts, including Moore himself, expect Moore’s Law to hold for some more time.

However, the exponentially increasing rate of circuit densification has continued into the present as shown in Table 1.2^[14]. The Pentium 4 microprocessor contains 42 million transistors connected to each other on a single piece of silicon. The increases in packing density of the circuitry are achieved by shrinking the line widths of the metal interconnects, by decreasing the size