



“十二五”普通高等教育本科国家级规划教材

纳米材料基础

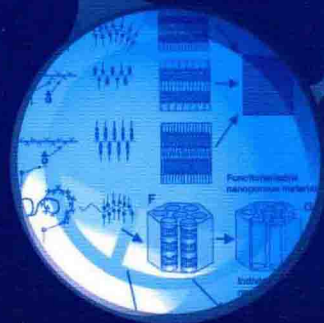
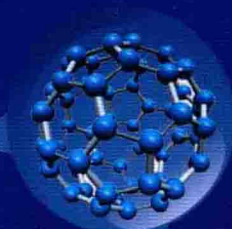
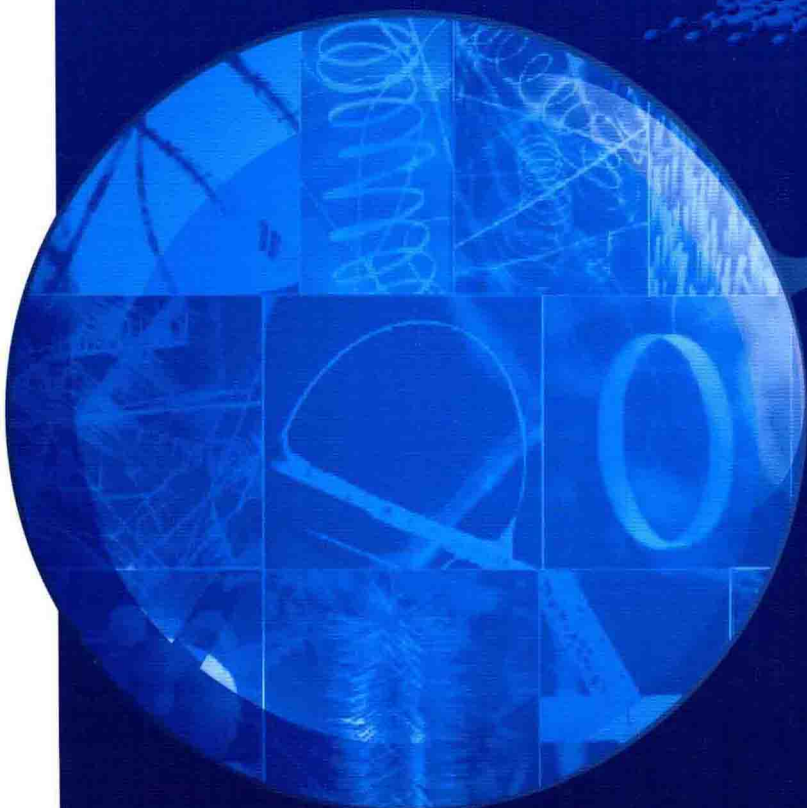
Fundamentals of Nanomaterials

(双语版)

The Second Edition

第二版

张耀君 编著



化学工业出版社



“十二五”普通高等教育本科国家级规划教材

Fundamentals of Nanomaterials

纳米材料基础

(双语版)

第二版

张耀君 编著



化学工业出版社

· 北京 ·

定价：32.80元

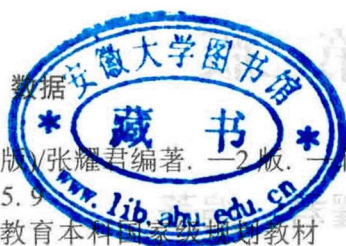
32.80元

本书为“十二五”普通高等教育本科国家级规划教材。

为使学生更好地掌握纳米材料的基本概念及基础知识,增强学生跨文化进行专业交流的能力,亦为学生以后阅读专业文献、撰写科研论文做铺垫,本书以中英双语的形式呈现;每章均以英文部分开篇,随后附有专业词汇的音标及释义,然后是对英文部分的中文翻译,以方便学生理解。全书共分为八章,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章为纳米效应的相关概念。第3章是关于纳米材料的力学、热学、磁学及光学性能。第4章重点介绍了“自上而下”和“自下而上”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章是碳纳米材料的合成。第7章为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。

本书可作为高等院校材料类、化学类、化工类、环境类、能源类、电子类等专业的本科生和研究生教材,亦可供相关专业工程技术人员、科研人员参考。

图书在版编目(CIP)数据



纳米材料基础(双语版)/张耀君编著. —2版. —北京:
化学工业出版社, 2015.9

“十二五”普通高等教育本科国家级规划教材
ISBN 978-7-122-24343-0

I. ①纳… II. ①张… III. ①纳米材料-高等学校-
教材-汉、英 IV. ①TB383

中国版本图书馆CIP数据核字(2015)第129946号

责任编辑:宋林青
责任校对:宋 玮

装帧设计:王晓宇

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:高教社(天津)印务有限公司

787mm×1092mm 1/16 印张14½ 字数372千字 2015年9月北京第2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:29.80元

版权所有 违者必究

前 言

本书第一版于 2011 年正式出版发行后,多所院校选其作为教材,这是我和出版社都始料未及的。为不辜负读者的厚爱,每次重印时,我们均尽自己最大可能进一步提升本书的质量,但限于版面问题,每次都是“小修小补”。值本书入选“十二五”普通高等教育本科国家级规划教材之际,再加上纳米科技的发展也亟需更新、补充部分内容,所以推出了第二版。

本次再版延续了第一版由浅入深、循序渐进、注重基础、关注前沿的特色;全书内容新颖、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,侧重纳米科技的研究进展及最新成果,体现了基本理论与生产实际相结合的教育理念。

本次再版第 1 章增加了零维、一维、二维及三维系统中电子的运动行为,从理论上阐明了自由电子模型、能量与态密度之间的关系;细化了纳米结构的分类以及纳米结构中各符号的含义;增加了纳米材料在医疗,尤其是再生疗法中的应用。第 4 章增加了超临界水热合成、喷雾冷冻干燥技术、各向异性纳米粒子的合成和组装、一维纳米结构聚合物的合成。第 6 章增加了石墨烯的性能与制备。第 8 章增加了氢能经济的内容。

本书承蒙李聚源教授审阅,提出了许多宝贵的修改意见;王亚超、刘礼才、康乐、柴倩、杨梦阳、张力、张科等在翻译及生词列表等工作中给予了诸多帮助;化学工业出版社的编辑对本书的修订给予了大力支持;在此一并表示衷心的感谢。

限于作者水平,书中疏漏和不妥之处,敬请同行及读者批评指正。

编著者

2015 年 3 月 20 日于西安

第一版前言

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

CONTENTS

1. Introduction to Nanoscale Materials 1

1.1 Introduction to the nanoworld 1

1.2 Definition of nanoscale materials 1

1.2.1 Nanometer 1

1.2.2 Definition of nanoscale materials 2

1.3 Classification of nanoscale materials 3

1.3.1 According to the spatial dimension of materials 3

1.3.2 According to the quantum properties of materials 4

1.3.3 According to material properties 12

1.3.4 According to the shape and chemical composition 12

1.4 Nanoscale science and technology 17

1.5 Driven by industrial revolution 17

1.6 Fundamental limitations of present technologies 18

1.7 Molecular electronics 18

1.8 Technical challenges in future 18

1.9 Applications of nanomaterials 20

1.9.1 Water purification 20

1.9.2 Nanocatalysts 20

1.9.3 Nanosensors 20

1.9.4 Energy 21

1.9.5 Medical applications 21

References 23

Review questions 25

Vocabulary 25

1. 纳米材料概论 31

1.1 纳米世界概述 31

1.2 纳米材料的定义 31

1.2.1 纳米 31

1.2.2 纳米材料的定义 31

1.3 纳米材料的分类 32

1.3.1 依据材料的空间维度分类 32

1.3.2 依据材料的量子性质分类 32

1.3.3 依据材料的性能分类 37

1.3.4 依据形态和化学组成分类 37

1.4 纳米科学与技术 38

1.5 工业革命的驱动 39

1.6 目前技术的基础性缺陷 39

1.7 分子电子学 40

1.8 未来的技术挑战 40

1.9 纳米材料的应用 40

1.9.1 水的净化 41

1.9.2 纳米催化剂 41

1.9.3 纳米传感器 41

1.9.4 能源 41

1.9.5 医药中的应用 41

复习题 43

2. Nanometer Effects of Nanoscale Materials 44

2.1 Small size effect 44

2.2 Quantum size effect 45

2.2.1 Relationship between energy gap and particle size 45

2.2.2 Application 46

2.3 Surface effect 47

2.4 Macroscopic quantum tunnel effect 48

2.4.1 Ballistic transport 48

2.4.2 Tunneling 48

2.4.3 Resonance tunneling 49

2.4.4 Inelastic tunneling 50

2.4.5 Tunnel effect 50

2.4.6 Macroscopic quantum tunnel effect 50

References 51

Review questions 51

Vocabulary 52

2. 纳米材料的纳米效应 52

2.1 小尺寸效应 53

2.2 量子尺寸效应 53

2.2.1 能隙与粒子尺寸的关系 53

2.2.2 应用 54

2.3 表面效应 54

2.4 宏观量子隧道效应 55

2.4.1 弹道传输 55

2.4.2 隧穿 55

2.4.3 共振隧穿 55

2.4.4 非弹性隧穿 55

2.4.5 隧道效应	56	4.3.3 Laser ablation	80
2.4.6 宏观量子隧道效应	56	4.4 Chemical vapor deposition (CVD) method	80
复习题	56	4.5 Liquid phase synthesis method	82
3. Properties of Nanoscale Materials	57	4.5.1 Precipitation method	82
3.1 Mechanical properties	57	4.5.2 Solvothermal method	84
3.1.1 Positive Hall-Petch slopes	57	4.5.3 Freeze-drying method (Cryochemical synthesis method)	88
3.1.2 Negative Hall-Petch slopes	57	4.5.4 Sol-gel method	90
3.1.3 Positive and negative Hall-Petch slopes	58	4.5.5 Microemulsions method	93
3.2 Thermal properties	59	4.5.6 Microwave-assisted synthesis	96
3.3 Magnetic properties	59	4.5.7 Ultrasonic wave-assisted synthesis	97
3.4 Electronic properties	60	4.6 Synthesis of bulk materials by consolidation of nanopowders	98
3.5 Optical properties	62	4.6.1 Cold compaction	98
3.5.1 Photochemical and photophysical processes of nanomaterials	62	4.6.2 Warm compaction	98
3.5.2 Absorption and luminescence spectra	63	4.7 Template-assisted self-assembly nanostructured materials	99
3.5.3 Ultraviolet-visible absorption spectroscopy	63	4.7.1 Principles of self-assembly	99
References	64	4.7.2 Self-assembly of MCM-41	100
Review questions	65	4.8 Self-assembly of nanocrystals	101
Vocabulary	65	4.9 Synthesis and assembly of anisotropic nanoparticles	102
3. 纳米材料的性能	66	4.9.1 Anisotropic nanoparticles with feature size	102
3.1 力学性能	66	4.9.2 Rod-like particles	102
3.1.1 正的 Hall-Petch 斜率关系	67	4.9.3 Preparation of various shaped Pt nanoparticles	104
3.1.2 负的 Hall-Petch 斜率关系	67	4.9.4 Preparation of various shaped Rh nanoparticles	105
3.1.3 正-负 Hall-Petch 斜率关系	67	4.10 Synthesis of polymeric one dimensional nanostructures (ODNS)	106
3.2 热学性能	67	4.10.1 Electrospinning synthesis of polymer ODNS	106
3.3 磁学性能	68	4.10.2 Membrane/template-based synthesis of polymer ODNS	109
3.4 电学性能	68	4.10.3 Template-free synthesis of polymer ODNS	110
3.5 光学性能	69	4.11 Green nanosynthesis	111
3.5.1 纳米材料的光化学和光物理 过程	69	4.11.1 Prevent wastes	111
3.5.2 吸收光谱和发光光谱	69	4.11.2 Atom economy	112
3.5.3 紫外-可见吸收光谱	70	4.11.3 Using safer solvents	112
复习题	70	4.11.4 Enhance energy efficiency	112
4. Synthesis of Nanoscale Materials	71	References	112
4.1 "Top-down" and "bottom-up" approaches	71	Review questions	117
4.2 Solid phase method	72	Vocabulary	118
4.2.1 Mechanically milling	72		
4.2.2 Solid-state reaction	74		
4.3 Physical vapor deposition (PVD) method	75		
4.3.1 Thermal evaporation PVD method	75		
4.3.2 Plasma-assisted PVD method	77		

4. 纳米材料制备	123
4.1 “自上而下”和“自下而上”的合成方法	123
4.2 固相方法	124
4.2.1 机械磨	124
4.2.2 固相反应	124
4.3 物理气相沉积法 (PVD)	125
4.3.1 热蒸发 PVD 法	125
4.3.2 等离子体辅助 PVD 法	126
4.3.3 激光消融法	127
4.4 化学气相沉积法 (CVD)	127
4.5 液相合成方法	128
4.5.1 沉淀法	128
4.5.2 溶剂热法	129
4.5.3 冷冻干燥法 (低温化学合成法)	131
4.5.4 溶胶-凝胶法	132
4.5.5 微乳液方法	133
4.5.6 微波辅助合成	135
4.5.7 超声波辅助合成	135
4.6 通过固化纳米粉合成块材	136
4.6.1 冷压	136
4.6.2 热压	136
4.7 模板辅助自组装纳米结构材料	136
4.7.1 自组装原理	136
4.7.2 MCM-41 自组装	137
4.8 自组装纳米晶	137
4.9 各向异性纳米粒子的合成和组装	137
4.9.1 具有特征尺寸的各向异性纳米粒子	137
4.9.2 棒状粒子	138
4.9.3 各种形貌 Pt 纳米粒子的制备	138
4.9.4 制备各种形貌的铑 (Rh) 纳米粒子	139
4.10 一维纳米结构 (ODNS) 聚合物的合成	139
4.10.1 电纺丝法合成一维纳米结构 (ODNS) 聚合物	140
4.10.2 基于膜或基于模板的一维纳米结构 (ODNS) 聚合物的合成	141
4.10.3 无模板剂的一维纳米结构 (ODNS) 聚合物的合成	141
4.11 绿色纳米合成	142
4.11.1 防止废弃物	142
4.11.2 原子经济	143
4.11.3 使用更安全的溶剂	143
4.11.4 提高能源效率	143
复习题	143

5. Scanning Tunneling Microscope and Atomic Force Microscope	144
5.1 Scanning tunneling microscope (STM)	144
5.1.1 Basic principle of STM	144
5.1.2 Operation modes	145
5.1.3 Application of STM	145
5.2 Atomic force microscope (AFM)	146
5.2.1 Basic principle of AFM	146
5.2.2 Mode of operation of AFM	147
5.2.3 Application of AFM	148
References	149
Review questions	150
Vocabulary	150
5. 扫描隧道显微镜和原子力显微镜	151
5.1 扫描隧道显微镜 (STM)	151
5.1.1 STM 的基本原理	151
5.1.2 操作模式	151
5.1.3 STM 的应用	151
5.2 原子力显微镜 (AFM)	152
5.2.1 AFM 的基本原理	152
5.2.2 AFM 的操作模式	152
5.2.3 AFM 的应用	153
复习题	153
6. Synthesis of Carbon Nanomaterials	154
6.1 Carbon family	154
6.1.1 Graphite and diamond	154
6.1.2 Allotrope of carbon	154
6.2 Fullerenes	155
6.2.1 Synthesis of C ₆₀	155
6.2.2 Purification of fullerenes	157
6.2.3 Structure of C ₆₀	158
6.2.4 ¹³ C nuclear magnetic resonance spectroscopy	158
6.2.5 Endofullerenes	159
6.2.6 Nucleophilic addition reactions	160
6.2.7 Polymerization of C ₆₀	160
6.2.8 Fabrication of nanocar	161
6.3 Carbon nanotubes ^[45]	162
6.3.1 Synthesis of nanotubes	162
6.3.2 Growing mechanisms	166
6.3.3 Geometry of carbon nanotubes	167
6.4 Graphene	169
6.4.1 Properties of graphene	169
6.4.2 Synthesis of graphene	170
References	176
Review questions	179
Vocabulary	180

6. 碳纳米材料的合成.....182

6.1 碳族.....182	
6.1.1 石墨和金刚石.....182	
6.1.2 碳的同素异形体.....182	
6.2 富勒烯.....182	
6.2.1 C_{60} 的合成.....183	
6.2.2 富勒烯的提纯.....183	
6.2.3 C_{60} 的结构.....183	
6.2.4 ^{13}C 核磁共振谱.....184	
6.2.5 富勒烯包合物.....184	
6.2.6 亲核加成反应.....184	
6.2.7 C_{60} 的聚合反应.....184	
6.2.8 纳米车的制造.....184	
6.3 碳纳米管.....184	
6.3.1 碳纳米管的合成.....184	
6.3.2 生长机理.....185	
6.3.3 碳纳米管的几何构型.....186	
6.4 石墨烯.....186	
6.4.1 石墨烯的性质.....187	
6.4.2 石墨烯的合成.....187	
复习题.....190	

7. Lithography for Nanofabrication.....191

7.1 Microfabrication by photolithography of ultraviolet light.....191	
7.2 Nanofabrication by scanning beam lithography.....194	
7.2.1 Electron beam lithography.....194	
7.2.2 Focused ion beam lithography.....194	
7.3 Nanoimprint lithography.....195	
7.3.1 Nanoimprint lithography.....195	
7.3.2 Step-and-flash imprint lithography.....196	
7.3.3 Microcontact printing.....196	
7.4 Scanning probe lithography.....197	
References.....199	
Review questions.....200	
Vocabulary.....201	

7. 光刻技术用于纳米制造.....202

7.1 紫外线光刻微制造.....202	
7.2 扫描束刻蚀纳制造.....203	
7.2.1 电子束刻蚀.....203	
7.2.2 聚焦离子束刻蚀.....204	
7.3 纳米压印刻蚀技术.....204	
7.3.1 纳米压印刻蚀.....204	
7.3.2 步进式闪烁压印光刻.....204	
7.3.3 微接触印制.....205	
7.4 扫描探针刻蚀.....205	
复习题.....206	

8. Nanotechnology for Production of

Hydrogen by Solar Energy.....207	
8.1 Hydrogen economy.....207	
8.2 Hydrogen production.....208	
8.3 Conversion of solar energy.....209	
8.4 Hydrogen production by photocatalytic water splitting.....210	
8.5 Loading metal over TiO_2210	
8.6 Development of visible-light-driven photocatalysts.....211	
8.6.1 Loading Cr^{3+} over titanate nanotubes.....211	
8.6.2 Semiconductor composition.....212	
References.....216	
Review questions.....217	
Vocabulary.....217	
8. 纳米技术用于太阳能制氢.....218	
8.1 氢能经济.....219	
8.2 产氢.....219	
8.3 太阳能转换.....219	
8.4 光催化分解水制氢.....220	
8.5 TiO_2 上负载金属.....220	
8.6 可见光驱动的光催化剂的发展.....220	
8.6.1 在钛酸盐纳米管上负载 Cr^{3+}220	
8.6.2 半导体复合材料.....221	
复习题.....222	

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 Smally: “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

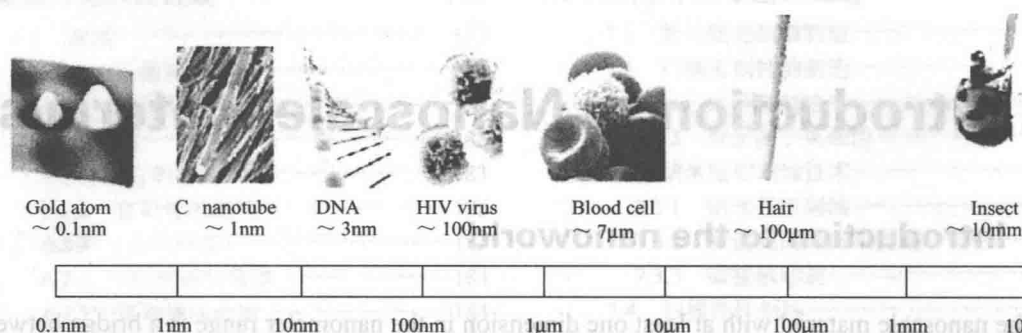


Fig.1.1 Length scale and some examples related^[2]

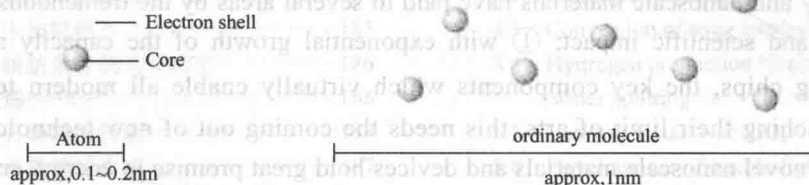


Fig.1.2 Schematic representation for atom and molecule

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.

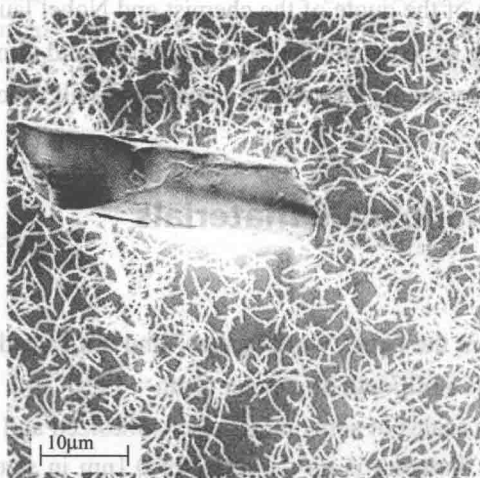


Fig.1.3 Human hair fragment and a network of single-walled carbon nanotubes

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 (<2nm), mesoporous (2~50nm) and macroporous (>50nm), 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 1μm 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 and Fig. 1.4^[1,3].

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

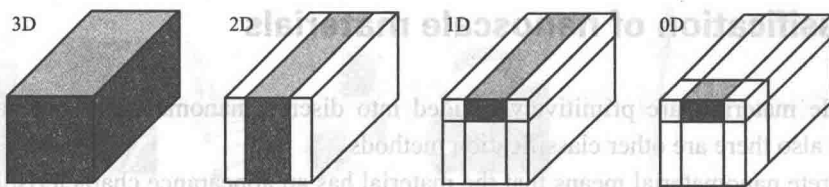


Fig.1.4 Dimensionality systems of three-dimension (3D), two-dimension (2D), one-dimension (1D) and zero-dimension (0D)

(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 (the material is dimensionless in three directions). 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 material is dimensionless in the other two directions). The system includes nanowires, nanorods, nanofilaments, nanotubes and etc. The ratio of the length to the diameter of these structures is called aspect ratio. The aspect ratio for nanorods generally lies in the range of 10~100. If aspect ratio of nanorods becomes more than 100, they are termed as nanowires. Nanowires are hence long nanorods. Nanotubes are on the other hand, nanorods with hollow interiors.

(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 d_x , d_y and d_z directions containing a number of “free” electrons. The “free” means those electrons are delocalized and not bound to individual atom.

In the free-electron model, each electron in the solid moves with a velocity $\vec{v} = (v_x, v_y, v_z)$.

The energy of an individual electron is then just its kinetic energy:

$$E = \frac{1}{2} m \vec{v}^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \quad (1.1)$$

According to Pauli’s exclusion principle, each electron must be in a unique quantum state. Since electrons can have two spin orientations ($m_s = +1/2$) and ($m_s = -1/2$), only two electrons with opposite spins can have the same velocity \vec{v} . This case is analogous to the Bohr model of atoms, in which each orbital can be occupied by two electrons at maximum. In solid-state physics, the wavevector $\vec{k} = (k_x, k_y, k_z)$ of a particle is more frequently used instead

of its velocity to describe the particle's state. Its absolute value $k = |\vec{k}|$ is the wavenumber. The wavevector \vec{k} is directly proportional to the linear momentum (\vec{p}) and thus also to the velocity (\vec{v}) of the electron.

The calculation of the energy states for a bulk crystal is based on the assumption of periodic boundary conditions. Periodic boundary conditions are a mathematical trick to "simulate" an infinite ($d = \infty$) solid. This assumption implies that the conditions at opposite borders of the solid are identical. In this way, an electron that is close to the border does not really "feel" the border. In other words, the electrons at the borders "behave" exactly as if they were in the bulk. This condition can be realized mathematically by imposing the following condition to the electron wavefunctions: $\psi(x, y, z) = \psi(x + d_x, y, z)$, $\psi(x, y, z) = \psi(x, y + d_y, z)$, and $\psi(x, y, z) = \psi(x, y, z + d_z)$. In other words, the wavefunctions must be periodic with a period equal to the whole extension of the solid [4,5]. Each function describes a free electron moving along one Cartesian coordinate. In the argument of the functions, $k_{x,y,z}$ is equal to $\pm n\Delta k = \pm n2\pi / d_{x,y,z}$ and n is an integer [4-6]. These solutions are waves that propagate along the negative and the positive direction, for $k_{x,y,z} > 0$ and $k_{x,y,z} < 0$, respectively. An important consequence of the periodic boundary conditions is that all the possible electronic states in the \vec{k} space are equally distributed. There is an easy way of visualizing this distribution in the ideal case of a one-dimensional free-electron model: there are two electrons ($m_s = \pm 1/2$) in the state $k_x = 0$ ($v_x = 0$), two electrons in the state $k_x = +\Delta k$ ($v_x = +\Delta v$), two electrons in the state $k_x = -\Delta k$ ($v_x = -\Delta v$), two electrons in the state $k_x = +2\Delta k$ ($v_x = +2\Delta v$) and so on.

For a three-dimensional bulk material we can follow an analogous scheme. Two electrons ($m_s = \pm 1/2$) can occupy each of the states $(k_x, k_y, k_z) = (\pm n_x \Delta k, \pm n_y \Delta k, \pm n_z \Delta k)$, again with $n_{x,y,z}$ being an integer. A sketch of this distribution is shown in Fig.1.5. We can easily visualize the occupied states in \vec{k} -space because all these states are included into a sphere whose radius is the wavenumber associated with the highest energy electrons. At the ground state, at 0 K, the radius of the sphere is the Fermi wavenumber k_F (Fermi velocity v_F). The Fermi energy $E_F \propto k_F^2$ is the energy of the last occupied electronic state. All electronic states with an energy $E \leq E_F$ are occupied, whereas all electronic states with higher energy $E > E_F$ are empty. In a solid, the allowed wave numbers are separated by $\Delta k = \pm n2\pi / d_{x,y,z}$. In a bulk material $d_{x,y,z}$ is large, and so Δk is very small. Then the sphere of states is filled quasi-continuously [4].

We need now to introduce the useful concept of the density of states $D_{3d}(k)$, which is the number of states per unit interval of wavenumbers. From this definition, $D_{3d}(k)\Delta k$ is the number of electrons in the solid with a wavenumber between k and $k + \Delta k$. If we know the density of states in a solid we can calculate, for instance, the total number of electrons having wavenumbers less than a given k_{\max} , which we will call $N(k_{\max})$. Obviously, $N(k_{\max})$ is equal to $\int_0^{k_{\max}} D_{3d}(k)dk$. In the ground state of the solid, all electrons have wavenumbers $k \leq k_F$, where k_F is the Fermi wavenumber. Since in a bulk solid the states are homogeneously distributed in

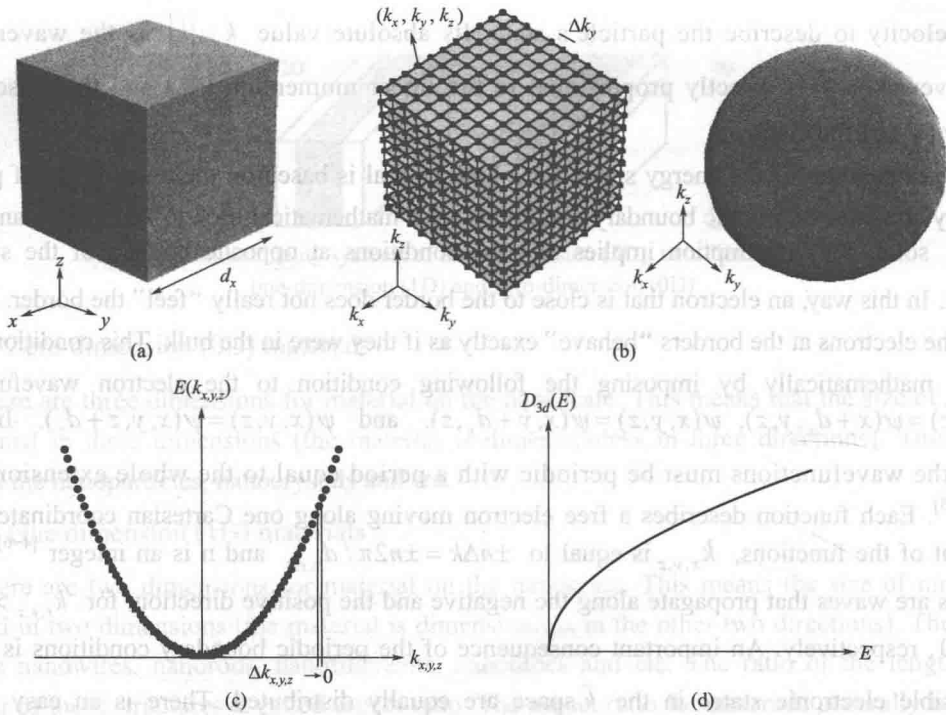


Fig.1.5 Electrons in a three-dimensional bulk solid^[5]

\bar{k} -space, we know that the number of states between k and $k + \Delta k$ is proportional to $k^2 \Delta k$ (Fig.1.5). This can be visualized in the following way. The volume in three-dimensional \bar{k} -space varies with k^3 . If we only want to count the number of states with a wavenumber between k and $k + \Delta k$, we need to determine the volume of a spherical shell with radius k and thickness Δk . This volume is proportional to product of the surface of the sphere (which varies as k^2) with the thickness of the shell (which is Δk). $D_{3d}(k) \Delta k$ is thus proportional to $k^2 \Delta k$, and in the limit when Δk approaches zero, we can write:

$$D_{3d}(k) = \frac{dN(k)}{dk} \propto k^2 \quad (1.2)$$

Instead of knowing the density of states in a given interval of wavenumbers it is more useful to know the number of electrons that have energies between E and $E + \Delta E$. We know that $E(k)$ is proportional to k^2 , and thus $k \propto \sqrt{E}$. Consequently, $dk / dE \propto 1 / \sqrt{E}$. By using Eq. (1.2), we obtain for the density of states for three-dimensional electron model^[5]:

$$D_{3d}(E) = \frac{dN(E)}{dE} = \frac{dN(k)}{dk} \frac{dk}{dE} \propto E \frac{1}{\sqrt{E}} \propto \sqrt{E} \quad (1.3)$$

This can be seen schematically in Fig.1.5. With Eq. (1.3) we conclude our simple description of a bulk solid. The possible states in which an electron can be found are quasi-continuous. The density of states varies with the square root of the energy.

Fig.1.5 shows electrons in a three-dimensional bulk solid. (a) Such a solid can be modeled as an infinite crystal along all three dimensions x, y, z . (b) The assumption of periodic boundary conditions yields standing waves as solutions for the Schrödinger equation for free electrons. The associated wavenumbers (k_x, k_y, k_z) are periodically distributed in the k -space^[5]. Each of the dots

shown in the figure represents a possible electronic state (k_x, k_y, k_z) . Each state in k -space can be only occupied by two electrons. In a large solid the spacing $\Delta k_{x,y,z}$ between individual electron states is very small, and therefore the k -space is quasi-continuously filled with states. A sphere with radius k_F includes all states with $k = (k_x^2 + k_y^2 + k_z^2)^{1/2} < k_F$. In the ground state, at 0 K, all states with $k < k_F$ are occupied by two electrons, and the other states are empty. Since the k -space is homogeneously filled with states, the number of states within a certain volume varies with k^3 . (c) It is the dispersion relation for free electrons in a three-dimensional solid. The energy of free electrons varies with the square of the wavenumber, and its dependence on k is described by a parabola. For a bulk solid the allowed states are quasi-continuously distributed and the distance between two adjacent states (here shown as points) in k -space is very small. (d) It is the density of states D_{3d} for free electrons in a three-dimensional system. The allowed energies are quasi-continuous and their density of states varies with the square root of the energy $E^{1/2}$ shown in Fig.1.5 [1].

(2) Quantum wells (2D)

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

When one or more dimensions of a solid become smaller than the De Broglie wavelength associated with the free charge carriers, an additional contribution of energy is required to confine the component of the motion of the carriers along this dimension. In addition, the movement of electrons along such a direction becomes quantized. This situation is shown in Fig.1.6. No electron can leave the solid, and electrons that move in the z -direction are trapped in a “box”. Mathematically this is described by infinitely high potential wells at the border $z = \pm \frac{1}{2} d_z$.

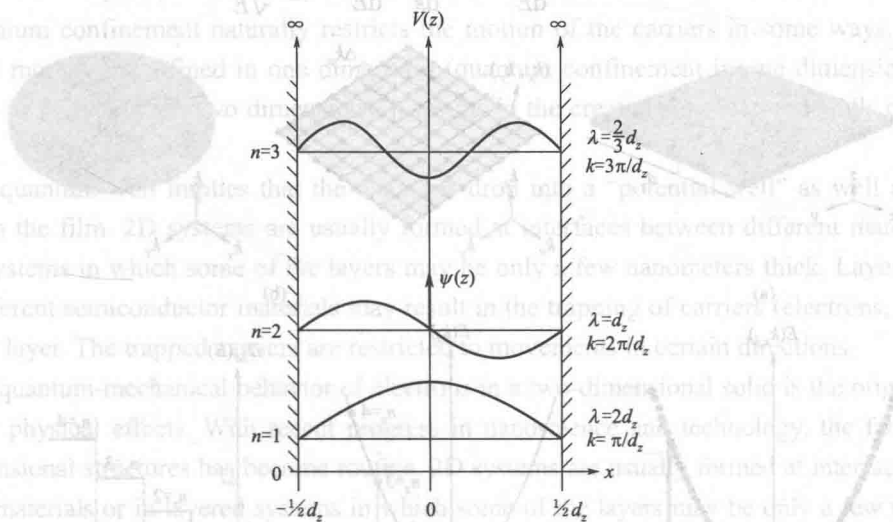


Fig.1.6 Particle-in-a-box model for a free electron moving along in the z -axis. The movement of electrons in the z -direction is limited to a “box” with thickness d : since electrons cannot “leave” the solid (the box), their potential energy $V(z)$ is zero within the solid, but is infinite at its borders.

The solutions for the particle-in-a-box situation can be obtained by solving the one-dimensional Schrödinger equation for an electron in a potential $V(z)$, which is zero within the box but infinite at the borders. As can be seen in Fig.1.6, the solutions are stationary waves with energies

$$E_{nz} = \hbar^2 k_z^2 / (2m) = \hbar^2 k_z^2 / (8\pi^2 m) = \hbar^2 n_z^2 / (8md_z^2), n_z = 1, 2, 3$$

This is similar to states $k_z = n_z \Delta k_z$ with $\Delta k_z = \pi / d_z$. Again, each of these states can be occupied at maximum by two electrons.

For a two-dimensional solid that the states in the k -space is extended in the x - y -plane only discrete values are allowed for k_z . The thinner the solid in the z -direction, the larger is the spacing Δk_z between these allowed states. On the other hand, the distribution of states in the k_x - k_y plane remains quasi-continuous. Therefore one can describe the possible states in the k -space as planes parallel to the k_x - and k_y -axes, with a separation Δk_z between the planes in the k_z -direction. We can number the individual planes with n_z . Since within one plane the number of states is quasi-continuous, the number of states is proportional to the area of the plane. This means that the number of states is proportional to $k^2 = k_x^2 + k_y^2$. The number of states in a ring with radius k and thickness Δk is therefore proportional to $k \Delta k$. Integration over all rings yields the total area of the plane in k -space. Here, in contrast to the case of a three-dimensional solid, the density of states varies linearly with k :

$$D_{2d}(k) = \frac{dN(k)}{dk} \propto k \tag{1.4}$$

In the ground state, all states with $k \leq k_F$ are occupied by two electrons. We now want to know how many states exist for electrons that have energies between E and $E + \Delta E$. We know the relation between k and E : $E(k) \propto k^2$ and thus $k \propto \sqrt{E}$ and $dk / dE \propto 1 / \sqrt{E}$. By using Eq. (1.4) we obtain the density of states for a 2-dimensional electron gas shown in Fig.1.7.

$$D_{2d}(E) = \frac{dN(E)}{dE} = \frac{dN(k)}{dk} \frac{dk}{dE} \propto \sqrt{E} \frac{1}{\sqrt{E}} \propto 1 \tag{1.5}$$

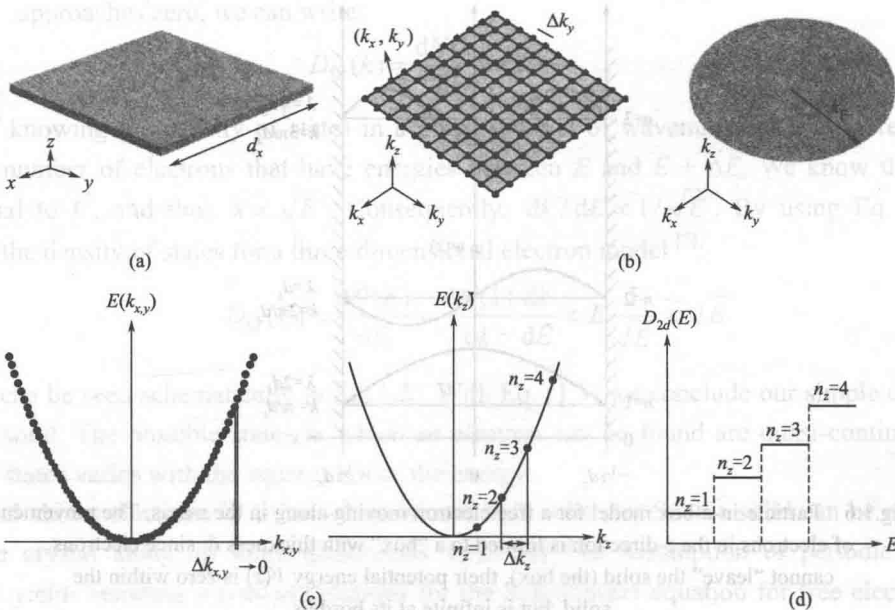


Fig.1.7 Electrons in a two-dimensional system.