

Donglu Shi

纳米生物医学

NanoScience
in Biomedicine



清华大学出版社

Springer

Editor-in-Chinef
Donglu Shi

纳米生物医学

NanoScience in Biomedicine



内 容 简 介

本书主要介绍了纳米生物医学研究领域的新进展。本书分为三部分，第一部分叙述了纳米尺度的生物材料的设计、合成、特性以及应用，包括干细胞和相关技术、聚合体纳米纤维及其生物医学应用、自组织生物材料及其生物医学应用、生物探测材料的合成和自组织、磷酸盐陶瓷的生物领域的应用、生物材料的表面和界面特性、碳纳米管在生物传感方面的应用等；第二部分详细介绍纳米尺度的生物医学的新技术，包括药物输运技术、生物医学领域的微纳技术、DNA技术、纳米尺度的生物活性表面和移植、碳纳米管智能材料在生物和医学方面的应用等。第三部分的重点是纳米材料合成和结构的最新进展，包括纳米材料中的声子行为、纳米粒子和纳米流体的合成和特性的最新进展等。

本书由工作在世界纳米生物医学领域的杰出科学家撰写。本书的读者对象为相关专业高年级大学生、研究生、科技人员、工程技术人员。

版权所有，侵权必究。侵权举报电话：010-62782989 13701121933

图书在版编目(CIP)数据

纳米生物医学 = NanoScience in Biomedicine: 英文/时东陆主编. —北京: 清华大学出版社, 2009.1

ISBN 978-7-302-17905-4

I. 纳… II. 时… III. ①纳米材料－英文 ②纳米材料－应用－生物医学工程－英文
IV. TB383 R318

中国版本图书馆 CIP 数据核字(2008)第 090804 号

责任编辑：韩燕丽 张 彤

责任校对：王淑云

责任印制：孟凡玉

出版发行：清华大学出版社 地 址：北京清华大学学研大厦 A 座

<http://www.tup.com.cn> 邮 编：100084

社 总 机：010-62770175 邮 购：010-62786544

投稿与读者服务：010-62776969,c-service@tup.tsinghua.edu.cn

质 量 反 馈：010-62772015,zhilang@tup.tsinghua.edu.cn

印 装 者：北京雅昌彩色印刷有限公司

经 销：全国新华书店

开 本：153×235 印 张：45.75 插 页：9 页 字 数：1055 千字

版 次：2009 年 1 月第 1 版 印 次：2009 年 1 月第 1 次印刷

书 号：ISBN 978-7-302-17905-4

ISBN 978-3-540-49660-1

印 数：1~1900

定 价：140.00 元

本书如存在文字不清、漏印、缺页、倒页、脱页等印装质量问题，请与清华大学出版社出版部联系调换。联系电话：(010)62770177 转 3103 产品编号：022844-01

Preface

The research on nanomaterials and nano biomedicine has been advancing rapidly in recent years, particularly in the development of unique nanostructures for specific biomedical applications. The research addresses the critical issues in medical applications including *in vivo* imaging, cell targeting, local drug delivery and treatment, bioactivity, compatibility, and toxicity. In the biomedical applications, traditional materials science and engineering have to deal with new challenges in the areas of synthesis, structure development, and biological, chemical, and physical behaviors, since medical needs place new demands in these respects.

The novel nanotechnologies included in this book are of great importance for biomedical applications. Based on these new developments, it is possible to alter the intrinsic properties of nanomaterials that cannot be achieved by conventional methods and materials. A key aspect of being able to manipulate the properties of the nanomaterials is the nanoscale architecture and engineering by various processing techniques. Some of the novel approaches introduced in this book can provide multi-functionality for a variety of substrates, be it biological, physical, or chemical, which can then be engineered for particular biomedical applications. For instance, novel surface functionalization methods have been developed for bio assays and cell targeting. In these approaches, a thin coating of polymer can be applied to the nano species and to provide various functional groups for passive or covalent coupling to biological molecules, such as antigens, antibodies, and DNA/RNA hybridization. However, the conventional synthesis of materials has only resulted in a single functionality which is generally not suitable for the complex procedures required for medical applications. The novel concept introduced in this book can be used to develop multiple functionalities, particularly suitable for medical diagnosis and treatment. The enhancement of properties is based on the study of the new nano structures and interfacial mechanisms.

This book summarizes the most recent research and development in nano biomedicine and addresses the critical issues in nanomaterials synthesis, structure, and properties. In particular, the major topics in nano biomedicine are covered in

this book. The book devotes three parts of 25 chapters to various aspects of nanomaterials and their medical applications. Detailed experimental procedures are presented at a level suitable for readers with no previous training in these areas.

The first part of the book concentrates on the research works of design, synthesis, properties, and applications of nano scale biomaterials. Chapter 1 is on the topics of stem cells and related nanotechnology. In Chapter 2, an overview is documented on the recent progress of polymer nanofibers, mostly electrospun in biomedical applications, along with a brief description of history, principle, and operating parameters of electrospinning process. Chapter 3 introduces new concepts in assembly of biomaterials. In view of the emerging importance of bio-inspired materials in medical applications, this chapter is focused on describing the fundamentals of intermolecular interactions and their applications in biomaterials science. The particular focus will be on processes and structures that mimic the natural ECM. Chapter 4 is on the fabrication and assembly of nanomaterials for biological detections. In Chapter 5, the authors first introduce the peptide design strategies for the construction of nanostructured materials. It then gives a brief tutorial of amino acid structure and function. It further describes higher-order assemblies of peptides and peptidomimetics. Chapter 6 introduces an important category of nanomaterials: quantum dots. Chapter 7 focuses on the phosphate ceramics for applications in bio-related fields. In this chapter, the authors briefly review the progress made in the last decade on the microwave-assisted synthesis and processing of biomaterials both in nanometer- and micrometer-size range. Chapter 8 introduces the characterization of biointerfaces and biosurfaces in biomaterials design. In Chapter 9, the authors bring the focus of the discussion to one of the important nanomaterials: carbon nanotubes and their applications in biosensing. Chapter 10 discusses the issues on heparin-conjugated nanointerfaces for biomedical applications.

The second part of the book is on the new nanotechnologies in biomedicine. In Chapter 11, the authors introduce some of the novel technologies in drug delivery. Chapter 12 reports unique experimental results on nano metal particles for biomedical applications. Chapter 13 is on the micro- and nanoscale technologies in high-throughput biomedical experimentation. Chapter 14 introduces delivery system of bioactive molecules for regenerative medicine. Chapter 15 gives an overview on modification of nano-sized materials for drug delivery. Chapter 16 is another chapter on drug delivery, however via a different approach. Chapter 17 is about most recent developments in DNA nanotechnology. A major objective in this chapter deals with the creation of ordered nanostructures for executing complex operations. Chapter 18 provides an overview on the nanoscale bioactive surfaces and endosseous implantology. Chapter 19 gives an overview of potential applications of carbon nanotube smart materials in biology and medicine.

The last part of the book concentrates on some of the most recent experimental results on the nanomaterials synthesis and structure developments. These include

the synthesis, properties, and application of intrinsically electroconducting nanoparticles of polypyrrole and pyrrole/sulfonic diphenylamine (20/80) Copolymers. Some studies focus on the fracture processes in advanced nanocrystalline and nanocomposite materials. Unique nano properties such as field emission of carbon nanotubes are also introduced. Finally, the book concludes by introducing some theoretical aspects of the nanomaterials. In this chapter, the authors develop microscopic modeling of phonon modes in semiconductor nanocrystals.

Chapter 20 is on the physical origins of phonon behaviors in nanocrystals. Chapter 21 gives an overview on computer simulations and theoretical modeling of fracture processes in nanocrystalline metals and ceramic nanocomposites. Chapter 22 describes a detailed experimental study on the fabrication, structures, unique properties, and wide application potential of novel conducting polypyrrole (PPY) nanoparticles and nanocomposites. Chapter 23 introduces some of the most recent developments in the fascinating carbon nanotubes. Chapter 24 reviews the progress in the flexible dye-sensitized nanostructured thin film solar cells (DSSCs). Chapter 25 presents recent results on the synthesis of magnetic nanoparticles (MNP) and various types of magnetic nanofluids (MNF) or ferrofluids, their structural properties and behaviors in an external magnetic field.

We hope that these chapters will provide timely and useful information for the progress of nanomaterials and their applications in biomedicine.

Contents

1 Stem Cells and Nanostructured Materials.....	1
1.1 Introduction	1
1.2 Interaction of Stem Cells with Nanotopographic Substrates.....	3
1.2.1 Cell Shape and the Cytoskeleton.....	4
1.2.2 Morphology, Attachment and Proliferation	5
1.2.3 Differentiation	6
1.2.4 Self-Assembling Peptide Nanofibers.....	8
1.2.5 Summary	8
1.3 Stem Cell Interactions with Nanoparticles	9
1.3.1 Nanoparticles as Contrast Agents.....	10
1.3.2 Nanoparticles as Vehicles	10
1.3.3 Effect of Internalized Nanoparticles.....	11
1.3.4 Summary	17
1.4 Conclusions.....	17
Acknowledgements	18
References	18
2 Biomedical Polymer Nanofibers for Emerging Technology	21
2.1 Introduction	21
2.2 Electrospinning Technology-History, Principle, Parameter	23
2.3 Functionalization of Nanofibers.....	25
2.3.1 Bulk Modification	25
2.3.2 Surface Modification	27
2.4 Biomedical Applications	29
2.4.1 Tissue-Engineered Scaffolds	29
2.4.2 Wound Dressing	35
2.4.3 Biomedical Devices and Implants	36
2.4.4 Drug Delivery System	37
2.4.5 Other Applications.....	38
2.5 Concluding Remark	39
Acknowledgement.....	39
References	40
3 Nanoscale Mechanisms for Assembly of Biomaterials	43
3.1 Introduction	43

3.2	Non-Covalent Intermolecular Interaction	45
3.2.1	Electrostatic Interaction.....	46
3.2.2	Hydrogen Bonding	50
3.2.3	Hydrophobic Interactions	50
3.2.4	Non-Covalent Interactions in Biological Systems.....	51
3.2.5	Summary	52
3.3	Approaches for Bioinspired Nanoscale Assembly of Biomaterials	52
3.3.1	Supramolecular Assembly Based Primarily on Ion-Ion Interactions.....	53
3.3.2	Assembly of Amphiphilic Biomaterials	55
3.3.3	Biomimetic Supramolecular Assembly Based on Hydrogen Bonding	57
3.3.4	Biomimetic Assembly Based on Affinity-Based Interactions....	58
3.3.5	Summary	59
3.4	Development of Biomaterials That Mimic The Natural ECM	59
3.4.1	Introduction	59
3.4.2	Non-Covalent Interactions in Natural Extracellular Matrices.....	60
3.4.3	Biomaterials That Mimic ECM Structures and Properties	61
3.5	Concluding remarks	70
	Acknowledgements	71
	References.....	71
4	Fabrication and Assembly of Nanomaterials and Nanostructures for Biological Detections	76
4.1	Introduction	76
4.2	Semiconductor Quantum Dots and Metal Nanoparticles	77
4.2.1	Principles of Semiconductor QDs and Metal Nanoparticle Biosensors	77
4.2.2	Fabrication of semiconductor QDs and metal nanoparticles for biosensors.....	80
4.2.3	Assembly of QD and Metal Nanoparticle Arrays for Biosensor Applications	81
4.3	Field Effect Sensors Based on Nanowires and Nanotubes.....	82
4.3.1	Detection Principles of 1-D Nanowire and Nanotube-Based Biosensors	82
4.3.2	Fabrication of 1-D Nanowires and Nanotubes	83
4.3.3	Assembly of Ordered Nanowire and Nanotube Arrays	85
4.3.4	Horizontally-Aligned Growth of Single-Walled Nanotubes (SWNTs) on Substrates	86
4.4	Micro-cantilever sensors	89
4.4.1	Detection Principle of Micro-Cantilever Sensors.....	89

4.4.2	Fabrication of the array of micro-cantilever sensors	90
4.5	Summary	91
	References.....	92
5	Nanostructured Materials Constructed from Polypeptides.....	96
5.1	Introduction	96
5.2	Amino Acids and Their Derivatives: Building Blocks for Nanostructured Materials	97
5.2.1	Canonical Amino Acids.....	97
5.2.2	Non-canonical Amino Acids.....	99
5.2.3	Peptidomimetics and Peptide Derivatives	100
5.3	Secondary, Tertiary, and Quaternary Structures in Nanomaterials ...	102
5.3.1	β -Sheet Fibrils	102
5.3.2	α -Helices and Coiled Coils	107
5.4	Materials Properties Arising from Peptide Construction.....	114
5.4.1	Stimulus-Responsiveness	114
5.4.2	Multifunctionality and Modularity	116
5.5	Technological Applications of Nanoscale Peptide Materials	119
5.5.1	Tissue Engineering and Regenerative Medicine	119
5.5.2	Antimicrobials	121
5.5.3	Controlled Drug Release	121
5.5.4	Nanoscale Electronics	122
5.6	Concluding Remarks	122
	References.....	123
6	Photoluminescent Carbon Nanomaterials: Properties and Potential Applications.....	128
6.1	Introduction	128
6.2	Photoluminescent Carbon Particles-Carbon Quantum Dots	130
6.3	Photoluminescent Carbon Nanotubes	135
6.3.1	A Consequence of Functionalization	136
6.3.2	Photoluminescence Features and Properties.....	137
6.3.3	Defect-Derived vs Band-Gap Emissions	143
6.4	Dots vs Tubes—Luminescence Polarization.....	144
6.5	Potential Applications	147
	Acknowledgement.....	150
	References.....	150
7	Microwave-assisted Synthesis and Processing of Biomaterials	154
7.1	Introduction	154
7.2	Synthesis of Hydroxyapatite	156
7.2.1	Synthesis in Aqueous Solution	157
7.2.2	Microwave-Hydrothermal Synthesis.....	162

7.2.3	Synthesis of HA by the Conversion of Precursor Monetite Prepared in Mixed Solvents	163
7.2.4	Prepration of HA Thin Film.....	165
7.2.5	Synthesis by Solid State Reaction	166
7.3	Synthesis of β -Tricalcium Phosphate (β -Ca ₃ (PO ₄) ₂).....	166
7.4	Synthesis of Calcium Carbonate (CaCO ₃)	167
7.5	Synthesis of Composite Biomaterials	171
7.6	Synthesis of Functionally Graded Bioactive Materials.....	173
7.7	Microwave Sintering of Biomaterials	174
	References	176
8	Characterizing Biointerfaces and Biosurfaces in Biomaterials Design.....	178
8.1	Introduction	178
8.2	Characterization of Biointerfaces	181
8.2.1	Surface and Interface Analysis Using Fourier Transform Infrared Spectroscopy	181
8.2.2	Surface and Interface Analysis Using Atomic Force Microscopy	183
8.2.3	X-ray Photoelectron Spectroscopy	187
8.2.4	Contact Angle	188
8.2.5	Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS).....	189
8.3	Nano-Structuring Surfaces	190
8.3.1	Nanotopology	191
8.3.2	Nanopatterning Surfaces with Biomolecules.....	192
8.4	Conclusions	195
	References	196
9	Carbon Nanotubes for Electrochemical and Electronic Biosensing Applications.....	205
9.1	Introduction	205
9.2	Design Principles of CNT-Based Biosensors	206
9.2.1	CNTs as Modifiers of Electrode Surfaces	206
9.2.2	CNT-Based Composite Electrodes	209
9.2.3	Nanoparticles Decorated CNT-Based Electrodes	210
9.2.4	CNTs as Key Sensing Elements	211
9.2.5	CNT-Based Biosensors with Immobilized Biological Molecules.....	212
9.3	Electrochemical Detection of Biomolecules	218
9.3.1	Assessment Criteria of Sensors	224
9.3.2	Electrochemical Biosensors.....	224
9.4	Field-Effect Transistors Based on SWNTs.....	236

9.4.1	Protein Recognition	237
9.4.2	DNA Hybridization	239
9.4.3	Enzymatic Study.....	240
9.4.4	Protein Adsorption.....	240
9.4.5	Others	241
9.5	Conclusions and Future Prospects.....	241
	Acknowledgement.....	242
	Reference	242
10	Heparin-Conjugated Nanointerfaces for Biomedical Applications	247
10.1	Introduction.....	247
10.2	Heparin-Bound Biodegradable Polymers for Biocompatible Interfaces	249
10.2.1	Heparin-Conjugated Polylactide (PLA-Hep)	249
10.2.2	Heparin-Conjugated Star-Shaped PLA (sPLA-Hep).....	254
10.3	Heparin-Conjugated Polymeric Micelles	260
10.3.1	Synthesis of Tetronic®-PCL-Heparin Conjugate	260
10.3.2	Preparation of bFGF Loaded Polymeric Micelle	262
10.3.3	bFGF Release Study	264
10.3.4	Bioactivity of the Released bFGF	266
10.4	Heparin-Immobilized Small Intestinal Submucosa (SIS)	266
10.4.1	Preparation of Heparin-Immobilized SIS	266
10.4.2	Blood Compatibility Test	267
10.4.3	In Vitro Fibroblast Attachment.....	268
10.4.4	In Vivo Calcification	269
10.5	Conclusions.....	270
	References.....	270
11	Inorganic Nanoparticles for Biomedical Applications	272
11.1	Introduction	272
11.2	Unguided Drug Delivery Systems.....	274
11.2.1	Chemical Synthesis of Ceramic Nanomaterials	275
11.2.2	Functionalization of Ceramic Nanomaterials	276
11.3	Magnetically-Guided Drug Delivery Systems	277
11.3.1	Magnetic Guiding.....	277
11.3.2	Chemical Synthesis and Properties of Magnetic Nanostructures.....	277
11.3.3	Functionalization of Magnetic Nanoparticles.....	279
11.3.4	Biocompatibility of Magnetic Nanoparticles for Drug Delivery.....	280
11.4	Optically-Triggered Drug Delivery Systems.....	280
11.4.1	Chemical Synthesis and Properties of NIR-Sensitive Nanoparticles.....	281

11.4.2	Functionalization of NIR-Sensitive Nanoparticles	282
11.4.3	Biocompatibility of NIR-Sensitive Nanoparticles for Drug Delivery.....	282
11.5	Summary	284
	References.....	284
12	Nano Metal Particles for Biomedical Applications	290
12.1	NMPs as Contrast Agents for Bioimaging	290
12.2	Fluorescing NMPs.....	292
12.3	NMPs with High Plamon Field for Fluorescence Manipulation	293
12.3.1	NMPs Used for Fluorescence Quenching	294
12.3.2	NMP for Fluorescence Enhancement in Biosensing	295
12.3.3	NMP for Fluorescence Enhancement in Bioimaging	301
12.4	Magnetic NMPs for Bioseparation.....	302
12.5	Magnetic NMPs for Biosensing	303
12.6	Magnetic NMPs for Cancer Hyperthermia	305
12.7	MultiFunctional NMPs	308
12.8	Conclusions	310
	Acknowledgements	310
	References.....	310
13	Micro- and Nanoscale Technologies in High- Throughput Biomedical Experimentation	314
13.1	Introduction.....	315
13.2	Microarray Technologies	316
13.2.1	Evolution of Microarrays	317
13.2.2	Microarray Fabrication and Applications.....	318
13.2.3	DNA and cDNA Microarrays	321
13.2.4	Protein and Antibody-Based Microarrays	323
13.2.5	Cell-Based Microarrays.....	325
13.2.6	Other Microarrays and Microarray-Based Diagnostics....	326
13.3	Micro- and Nanoengineering for Biomedical Experimentation....	327
13.4	Microfluidics	329
13.5	Other Micro- and Nanoscale Technologies for Biological and Chemical Detection.....	333
13.6	Conclusions	336
	Acknowledgements	336
	References.....	337
14	Delivery System of Bioactive Molecules for Regenerative Medicine	347
14.1	Introduction.....	347
14.2	Delivery Systems of Bioactive Molecules	348

14.2.1	Importance of Bioactive Molecules Release System for the Regenerative Medicine.....	348
14.2.2	Scaffold System.....	353
14.2.3	Injectable Hydrogel System	356
14.2.4	Microspheres System	357
14.2.5	Nanofiber Scaffold System	358
14.3	Differentiation of Adult Stem Cells Using Delivery System of Bioactive Molecules	359
14.3.1	Osteoegensis of MSC	359
14.3.2	Chondrogenesis of MSCs.....	360
14.4	Repair of Diaphyseal Long Bone Defect with Calcitriol Released Delivery Vehicle and MSCs.....	361
14.5	Future Directions	364
14.6	Conclusion	365
	Acknowledgements.....	365
	References.....	365
15	Modification of Nano-sized Materials for Drug Delivery	369
15.1	Introduction.....	369
15.2	Available Methods to Modify Nano-Sized Materials for Drug Delivery	371
15.2.1	Surface Modification.....	371
15.2.2	Shell-Core Modification.....	374
15.2.3	Bulk Modifications.....	374
15.3	Applications for Drug Delivery of Modified Nano Sized Biomaterials.....	375
15.3.1	Long Circulating Delivery.....	375
15.3.2	Targeting Delivery.....	378
15.3.3	New Therapy and Drug Carriers	382
15.4	Conclusions.....	384
	Acknowledgements.....	384
	References.....	384
16	Polymeric Nano Micelles as a Drug Carrier	388
16.1	Introduction.....	388
16.2	Self-Assembly and Micellization of Amphiphilic Block Copolymers.....	389
16.2.1	Amphiphilic Block Copolymers.....	389
16.2.2	Micellization of Amphiphilic Block Copolymers	390
16.2.3	Polymeric Micelle Shape.....	391
16.2.4	Characterization of Polymeric Micelle Size.....	392
16.2.5	CMC Determination of Polymeric Micelles.....	393

16.3	Drug Loaded Polymeric Micelles	395
16.3.1	Drug Incorporation in Polymeric Micelles.....	395
16.3.2	Drug Solubilization Capacity of the Polymeric Micelles	396
16.3.3	Drug Partitioning in Polymeric Micelles.....	396
16.3.4	Drug Release from Polymeric Micelles	397
16.4	Biological Applications of Polymeric Micelles	398
16.4.1	Biodistribution.....	398
16.4.2	Accumulation in Target Solid Tumors.....	399
16.5	Conclusions and Outlook	399
	References.....	400
17	DNA Nanotechnology	405
17.1	Introduction.....	405
17.2	Basic Features of DNA	406
17.3	Self-Assembly of DNA Aanostructures	407
17.3.1	Basic Concepts	407
17.3.2	Two-Dimensional DNA Array Structures.....	408
17.3.3	Three-Dimensional DNA Nanostructures	413
17.4	Self-Assembly Properties of DNA Nanostructures.....	414
17.4.1	DNA Templatated Self-Assembly of Biological Molecules.....	415
17.4.2	DNA-Templated Self-Assembly of Nanoscale Devices	419
17.5	Application of DNA-Based Nanotechnology	419
17.6	Conclusions and Outlook	423
	References.....	424
18	Nanoscale Bioactive Surfaces and Endosseous Implantology.....	428
18.1	Introduction.....	428
18.2	Peri-implant Endosseous Healing and Osseointegration.....	429
18.2.1	Peri-Implant Endosseous Healing	429
18.2.2	Effect of Implant Surface Characteristics on Osseointegration.....	431
18.2.3	Potential Advantage of Nanoscale Surfaces	432
18.3	Nanoscale Bioactive Surfaces	434
18.3.1	Nanoscale Textured Surface	434
18.3.2	Nanoscale Biological Molecules	439
18.3.3	Nanoscale Bioactive Calcium Phosphate Coating.....	440
18.4	Summary	444
	Acknowledgements	444
	References.....	444

19	Carbon Nanotube Smart Materials for Biology and Medicine.....	451
19.1	Introduction.....	451
19.2	Carbon Nanotube Array Synthesis.....	453
19.2.1	Array Synthesis	453
19.2.2	Synthesis of Carbon Nanotube Towers	454
19.2.3	CNT Array Nanoskin and Nanostrands	455
19.3	Properties of Carbon Nanotube Arrays	457
19.3.1	Hydrophobic Property	457
19.3.2	Electrowetting Property.....	458
19.3.3	Capillarity Property	459
19.3.4	Nanotube Array Actuator	460
19.4	Potential Applications of Nanotube Arrays In Biology and Medicine	463
19.4.1	Electronic Biosensors.....	464
19.4.2	Nanotube Electrodes for Biovoltage and Chemical Sensing.....	467
19.4.3	Carbon Nanotube Sensor Film for Environmental Monitoring.....	468
19.4.4	Nanocomposite Materials for Biological Applications	469
19.4.5	In-Body Biosensors: Optimistic Hopes and Wildest Outlook.....	472
19.4.6	Investigating Neuronal Activity and Function Using Nanotubes.....	475
19.5	Conclusions.....	480
	Acknowledgement	480
	References.....	480
20	Microscopic Modeling of Phonon Modes in Semiconductor Nanocrystals.....	485
20.1	Introduction.....	485
20.2	Theory	488
20.2.1	The Valence Force Field Model	488
20.2.2	Application of Group Theory to the Study of Nanocrystals	490
20.2.3	The Bond Charge Approximation	496
20.2.4	Lamb Modes.....	498
20.3	Results and Discussion.....	501
20.3.1	Phonon Density of States for Nanocrystals	501
20.3.2	Raman Intensities	504
20.3.3	Size Effects on the Highest Phonon Frequencies of Si.....	505

20.3.4	Size Effects on the Lowest Frequencies Phonon for Si.....	508
20.3.5	Folding of Acoustic Phonons	509
20.3.6	Size Effects on Si Raman Peaks.....	510
20.3.7	Size Effects on Mode Mixing.....	511
20.3.8	Size Effects on the Intensities of Ge Raman Peaks	511
20.3.9	Size Effects on the Highest Raman Frequencies for Ge with Fixed or Free Surfaces.....	513
20.3.10	Existence of Interface Modes for Nanocrystals with Fixed Surfaces	515
20.4	Correspondence between the Microscopic and Macroscopic Active Raman Modes.....	516
20.4.1	Projection of the Lamb Modes	516
20.4.2	Group Theory Prediction of the Raman Intensities of the Lamb Modes.....	518
20.4.3	Identifying Lamb Modes within the VFFM-Determined Modes.....	518
20.4.4	The Radial Distribution Function of Ge Nanocrystals	523
20.4.5	Raman Intensities for Ge NC and Lamb modes.....	523
20.5	Conclusions.....	527
	Acknowledgements.....	528
	Appendices.....	528
A.1	The Irreducible Matrices of the T_d Group Used in Our Calculations are as Follows.....	528
A.2	Displacements for the $l = 1$ Spheroidal Lamb Modes	529
A.3	Displacements for $l = 2$ Spheroidal Lamb Modes.....	530
A.4	Displacements for the $l = 2$ Torsional Lamb Modes.....	532
A.5	Displacements for the $l = 3$ Torsional Lamb Modes.....	533
A.6	Displacements for the $l = 4$ Torsional Lamb Modes.....	534
	References.....	535
21	Fracture Processes in Advanced Nanocrystalline and Nanocomposite Materials	537
21.1	Introduction.....	537
21.2	Specific Structural Features and Plastic Deformation Behavior of Nanomaterials.....	538
21.3	Brittle and Ductile Fracture Processes in Nanomaterials.....	543
21.4	Nucleation of Nanocracks at Grain Boundaries and Their Triple Junctions.....	547
21.5	Intergranular Brittle Fracture Through Nucleation and Convergence of Nanocracks in Nanomaterials.....	555
21.6	Crack Growth in Nanomaterials. Toughening Mechanisms.....	558
21.7	Concluding Remarks.....	563

Acknowledgements.....	564
References.....	564
22 Synthesis, Properties and Application of Conducting PPY Nanoparticles	568
22.1 Introduction.....	569
22.1.1 Synthesis of PPY Nanoparticles.....	569
22.1.2 Properties and Application of PPY Nanoparticles.....	573
22.2 Experimental.....	580
22.2.1 Materials.....	580
22.2.2 Polymerization	580
22.2.3 Characterization	580
22.3 Results and Discussion.....	581
22.3.1 The Effect of Polymerization Temperature on the Yield of the Nanoparticles.....	581
22.3.2 Size and Its Distribution of the PY/SD Copolymer Nanoparticles.....	582
22.3.3 Morphology of the PY/SD Copolymer Nanoparticles	583
22.3.4 Mechanism of the Formation and Self-Stabilization of the Nanoparticles.....	584
22.3.5 Bulk Electrical Conductivity	584
22.4 Conclusions.....	584
Acknowledgements.....	585
References.....	585
23 Field Emission of Carbon Nanotubes	588
23.1 Introduction.....	588
23.2 Field Emission	589
23.3 Carbon Nanotube Growth Technologies	592
23.4 Characterization of Field Emission From CNTs	599
23.4.1 Effect of Structure on Field Emission	600
23.4.2 Effect of Length and Space	601
23.4.3 Method of field emission enhancement.....	606
23.4.4 Gated Field-Emission Arrays with Carbon Nanotubes.....	610
23.5 Summary	614
Acknowledgement	614
References.....	614
24 Flexible Dye-Sensitized Nano-Porous Films Soar Cells.....	618
24.1 Introduction.....	618
24.2 Flexible DSSCs and Low Temperature Preparation.....	622