

## Contents

Preface XVII

List of Contributors XXI

Part One Copper, Silver and Gold Nanomaterials 1

- 1 Approaches to Synthesis and Characterization of Spherical and Anisotropic Copper Nanomaterials 3  
*Nicola Cioffi, Nicoletta Ditaranto, Luisa Torsi and Luigia Sabbatini*
- 1.1 Introduction 3
- 1.2 Physical/Mechanical and Vapor-Phase Approaches 7
- 1.2.1 Mechanical and Mechanochemical Milling 7
- 1.2.2 Electrical Wire Explosion and Electrospinning Approaches 8
- 1.2.3 Spray and Flame-Spray Pyrolysis 9
- 1.2.4 Arc-Discharge Approaches 10
- 1.2.5 Metal Vapor Condensation 12
- 1.2.6 Metal–Organic Chemical Vapor Condensation 12
- 1.3 Chemical Approaches 13
- 1.3.1 Wet-Chemical Routes without Surfactants 14
- 1.3.2 Wet-Chemical Routes Based on Surfactants and Low-Molecular-Weight Capping Agents 14
- 1.3.2.1 Aerosol OT (AOT)-Capped Cu Nanomaterials 14
- 1.3.2.2 Alkyl-Phosphate-Capped Cu NPs 22
- 1.3.2.3 Alkyl-Sulfate-Capped Cu NPs 22
- 1.3.2.4 Alkyl-Thiol-Capped Cu NPs 22
- 1.3.2.5 Cu NPs Capped by Quaternary Ammonium Surfactants 25
- 1.3.2.6 Cu NPs Capped by Nonionic Surfactants or Stabilizers 25
- 1.3.2.7 Cu NPs Capped by Cysteine, Oleic Acid and Other Small Molecules with Biological Relevance 26
- 1.3.3 Wet-Chemical Routes Based on Polymer and Dendrimer Capping Agents 28
- 1.3.3.1 The Polyol Process 30
- 1.3.3.2 Polymer-Based Soft-Template Processes 30
- 1.3.3.3 Encapsulation in Dendrimers 31

1.3.4	Wet-Chemical Routes Based on Biotemplate Systems	32
1.3.5	Redox Routes in Compressed and Heated Fluids: Hydrothermal, Solvothermal and Supercritical Fluid Methods	33
1.3.5.1	Hydrothermal Routes	33
1.3.5.2	Solvothermal Routes	34
1.3.5.3	Routes Based on Supercritical Fluids	34
1.3.6	Redox Routes in Ionic Liquids	37
1.3.7	Ultrasonic-Chemical Processes	38
1.4	Photochemical, Laser Ablation and Radiation- or Electron Beam-Assisted Processes	38
1.4.1	Photochemical Reduction in the Presence of Capping Agents and Sensitizers	39
1.4.2	Laser Ablation and Photo-Fragmentation Processes	40
1.4.3	$\gamma$ -Irradiation	41
1.4.4	Electron Beam Irradiation	42
1.5	Electrochemical Approaches	42
1.5.1	Sacrificial Anode Electrolysis in the Presence of Surfactants	43
1.5.2	Electrochemical Milling	46
1.5.3	Ultrasonic-Electrochemical	46
1.5.4	Electrolysis in Ionic Liquids	48
1.5.5	Template-Assisted Electrochemical Growth of Cu Nanorods and Nanowires	48
1.6	Conclusions	49
	References	51

## 2 Spherical and Anisotropic Copper Nanomaterials in Medical Diagnosis 71

*Chi-Chung Chou, Jen-Lin Chang and Jyh-Myng Zen*

2.1	Introduction	71
2.2	Copper Nanoparticles	73
2.3	Synthesis of Copper Nanoparticles	75
2.3.1	Chemical Reduction in Aqueous Media	75
2.3.2	Chemical Reduction in Organic Media	76
2.3.3	Photoreduction	77
2.3.4	Sonochemical Production	77
2.3.5	Machine-Chemical Reduction	78
2.3.6	Electrochemical Reduction	78
2.4	Applications of Cu-NPs in Medical Diagnosis	80
2.4.1	Medical Imaging	80
2.4.1.1	Magnetic Resonance Imaging	80
2.4.1.2	Positron Emission Tomography (PET)	81
2.4.2	Diagnosis of Metabolic Disorders	81
2.4.2.1	Glucose	81

2.4.2.2	Organic Acids	82
2.4.2.3	Amino Acids	83
2.4.2.4	Urate and Uric Acid	85
2.4.3	Other Medical Applications	85
2.4.3.1	Drug Delivery and Therapy	85
2.4.3.2	Antibacterial Activity	86
2.5	Conclusions	87
	References	89

### **3 Approaches to the Synthesis and Characterization of Spherical and Anisotropic Silver Nanomaterials 99**

*Deirdre M. Ledwith, Damian Aherne and John M. Kelly*

3.1	Introduction	99
3.2	Optical Properties of Metal Nanoparticles	99
3.3	Preparation of Spherical Nanoparticles	101
3.3.1	Stability of Electrostatically Stabilized Nanoparticles	101
3.3.2	Aqueous Synthetic Methods	103
3.3.2.1	Chemical Reduction	103
3.3.2.2	Physical Methods	104
3.3.3	Organic Solvents	106
3.3.3.1	Stability of Sterically Stabilized Nanoparticles	106
3.3.3.2	Reduction by the Solvent	107
3.3.3.3	Microemulsion Methods	107
3.3.3.4	Thiol-Stabilized Nanoparticles	109
3.4	Synthesis of Anisotropic Silver Nanoparticles	109
3.4.1	Nanorods and Nanowires	110
3.4.1.1	Aqueous Surfactant-Based Methods	111
3.4.1.2	Organic (Polyol-Based) Methods	113
3.4.2	Cubes	117
3.4.2.1	Aqueous Surfactant-Based Methods	117
3.4.2.2	Organic Polyol-Based Methods	117
3.4.3	Other Morphologies Prepared by the Polyol Process	119
3.4.3.1	Right Bipyramids	119
3.4.3.2	Nanobeams	120
3.4.3.3	Nanobars and Nanorice	120
3.4.4	Nanoplates and Nanoprisms	122
3.4.4.1	Photochemical Methods	122
3.4.4.2	Thermal Methods	127
3.4.4.3	Physical Aspects	133
3.5	Applications	137
3.6	Conclusions	137
	Abbreviations	138
	References	139

<b>4</b>	<b>Spherical and Anisotropic Silver Nanomaterials in Medical Therapy</b>	<b>149</b>
	<i>Kenneth K. Y. Wong</i>	
4.1	Introduction	149
4.2	Actions of Silver Nanoparticles	150
4.2.1	Antimicrobial Effects	150
4.2.2	Anti-Inflammatory Effects	151
4.3	Applications of Silver Nanoparticles in Medicine	152
4.3.1	Nanosilver in Diagnosis, Imaging and Targeting	152
4.3.2	Nanosilver in Therapeutics	154
4.3.2.1	Wound Dressings	154
4.3.2.2	Silver-Impregnated Catheters	155
4.3.2.3	Orthopedic Applications	157
4.3.2.4	Surgical Mesh	158
4.3.2.5	Disinfectants	159
4.4	Are Silver Nanoparticles Toxic?	159
4.4.1	Access via the Skin	160
4.4.2	Pulmonary Entry	161
4.4.3	Gastrointestinal Tract	162
4.4.4	Other Tissues	162
4.5	Possible New Therapeutic Options	163
4.5.1	Anti-Inflammatory Agents	163
4.5.2	Anti-Viral Drugs	163
4.6	Conclusions	164
	References	166
<b>5</b>	<b>Spherical and Anisotropic Silver Nanomaterials in Medical Diagnosis</b>	<b>173</b>
	<i>Yiping Zhao and Ralph A. Tripp</i>	
5.1	Introduction	173
5.2	Silver Nanostructure-Based Diagnostic Techniques	176
5.2.1	Surface Plasmon Resonance (SPR)	177
5.2.2	Localized Surface Plasmon Resonance (LSPR)	178
5.2.3	Metal-Enhanced Fluorescence	181
5.2.4	Surface-Enhanced Infrared Absorbance Spectroscopy	182
5.2.5	Surface-Enhanced Raman Spectroscopy	183
5.3	Overview of Ag Nanostructure Synthesis and Fabrication	185
5.3.1	Individual Metallic Nanoparticles	185
5.3.2	Aggregates of Metallic Nanoparticles	186
5.3.3	Arrays of Metallic Nanoparticles	186
5.4	Applications	190
5.4.1	Small Biomolecule Detection	192
5.4.2	Detection of MicroRNAs as Biomarkers of Disease	193
5.4.3	Nucleic Acids (DNA and RNA) Detection	196
5.4.4	Virus Detection	198

5.4.4.1	Using SERS to Distinguish between Different Virus Types	198
5.4.4.2	Using SERS to Detect Viruses in Biological Media	198
5.4.4.3	Using SERS to Detect Very Low Levels of Virus	200
5.4.4.4	Using SERS to Differentiate between Strains of a Single Virus Type	200
5.4.5	Bacteria Detection	201
5.4.5.1	Using SERS to Differentiate between Types of Bacteria	203
5.4.5.2	Using SERS to Differentiate between Different Bacterial Strains	205
5.4.5.3	Using SERS to Distinguish between Live and Dead Bacteria	206
5.4.5.4	SERS has Single-Bacterium Detection Sensitivity	207
5.5	Conclusions	208
	Acknowledgments	209
	References	209
<b>6</b>	<b>Health and Environmental Impact of Silver Nanomaterials</b>	<b>225</b>
	<i>Il Je Yu and Bruce Kelman</i>	
6.1	Introduction	225
6.2	Antimicrobial Activity	225
6.3	<i>In Vitro</i> Toxicity	227
6.3.1	Liver Cells	227
6.3.2	Neuronal Cells	227
6.3.3	Germ Cells	228
6.3.4	Peripheral Mononuclear Cells	229
6.4	<i>In Vivo</i> Toxicity	229
6.4.1	<i>In Vivo</i> Toxicity in Birds	229
6.4.2	<i>In Vivo</i> Genotoxicity in Rodents	229
6.4.3	Acute Toxicity in Rodents	230
6.4.4	28-Day Repeated Oral Dose Studies in Rodents	230
6.4.5	28-Day Inhalation Studies in Rodents	231
6.4.6	90-Day Inhalation Toxicity Study in Rodents	231
6.5	Environmental Exposure and Risk from Silver Nanoparticles	232
6.6	Conclusions	232
	References	233
<b>7</b>	<b>Approaches to Synthesis and Characterization of Spherical and Anisotropic Gold Nanomaterials</b>	<b>235</b>
	<i>Tai Hwan Ha</i>	
7.1	Introduction	235
7.2	Optical Properties of Gold Nanocrystals	236
7.3	Chemical Constituents for the Growth of Gold Nanocrystal	238
7.3.1	Gold Precursors	238
7.3.2	Influences of Reducing Agents	240
7.3.3	Influences of the Reaction Medium	241
7.3.4	Roles of Passivation Components	242

7.3.5	Hard Templates for the Fabrication of Anisotropic Nanomaterials	243
7.4	Representative Reactions Categorized by Reducing Agents	244
7.4.1	Fast Reduction by Sodium Borohydride	244
7.4.2	Polyol Synthesis in the Presence of PVP	245
7.4.2.1	Influences of Reaction Medium	245
7.4.2.2	Influences of Silver Ions and PVP	247
7.4.3	Other Thermal Reductions of Gold Precursors	248
7.4.3.1	Citrate Reduction in the Presence of PVP	248
7.4.3.2	DMF Reduction in the Presence of PVP	249
7.4.3.3	Amine Reduction	251
7.4.4	Seed-Mediated Growth by Ascorbic Acid	252
7.4.4.1	Overview of Seed-Mediated Growth	253
7.4.4.2	Controversial Issues with the Seed-Mediated Growth	254
7.4.4.3	Influences of Silver and Halide Ions	255
7.4.5	Electrochemical and Photochemical Growth of Gold Nanocrystals	255
7.5	Morphologies of Representative Gold Nanocrystals and Possible Growth Mechanisms	256
7.5.1	Frequently Observed Morphologies of Gold Nanocrystals	256
7.5.1.1	Twinned Gold Nanorods and Related Decahedrons	256
7.5.1.2	Gold Icosahedrons and Nanoplates	257
7.5.1.3	Single Crystalline Gold Nanocrystals	258
7.5.1.4	Irregular Multipods	259
7.5.1.5	Post-Treatment of As-Grown Nanocrystals	259
7.5.1.6	Noticeable Features in the Observed Morphologies	260
7.5.2	Growth Mechanism of Gold Nanocrystals	261
7.5.2.1	Seed Structures at the Early Stage of Growth	261
7.5.2.2	Twinning and Reaction Temperature	262
7.5.2.3	Thermodynamic Stability of Twinned Particles	264
7.5.2.4	Roles of Passivating Chemicals in Shape Development	264
7.5.2.5	Influences of Surface-Active Chemicals	265
7.5.2.6	Overall Picture for the Growth of Gold Nanocrystals	266
7.6	Applications of Gold Nanocrystals in the Life Sciences	267
7.6.1	Contrast-Enhancing Agents	267
7.6.2	Photothermal Therapeutics	268
7.6.3	Renal Barrier and Cytotoxicity of Gold Nanomaterials	268
7.7	Summary and Perspectives	269
	Acknowledgment	270
	References	270
8	<b>Spherical and Anisotropic Gold Nanomaterials in Medical Therapy</b>	277
	<i>Takuro Niidome, Atsushi Shiotani, Yoshiki Katayama and Yasuro Niidome</i>	
8.1	Introduction	277
8.2	Gold Nanospheres	278

8.2.1	Cellular Imaging using Light Scattering from Gold Nanospheres	278
8.2.2	Gold Nanospheres as a Contrast Agent for Computed Tomography	278
8.2.3	Photothermal Cellular Damage	279
8.2.4	Radiofrequency Thermal Damage of Cells	279
8.2.5	DNA Carrier for Gene Therapy	281
8.3	Gold Nanoshells	283
8.4	Gold Nanorods	284
8.4.1	Preparation of Biocompatible Gold Nanorods	285
8.4.2	In Vitro Bioimaging and Photothermal Ablation of Cells	287
8.4.3	In Vivo Bioimaging	289
8.4.4	Photothermal Therapy	291
8.4.5	Drug Release System Responding to Laser Irradiation	292
8.4.6	Controller of Gene Expression	296
8.5	Other Anisotropic Gold Nanoparticles	297
8.6	Conclusions	298
	Acknowledgments	298
	References	298

## Part Two Palladium and Platinum Nanomaterials 303

<b>9</b>	<b>Approaches to Synthesis and Characterization of Spherical and Anisotropic Palladium Nanomaterials</b>	<i>305</i>
	<i>Ruel G. Freemantle, Minghong Liu, Wen Guo and Sherine O. Obare</i>	
9.1	Introduction	305
9.2	Synthesis	306
9.2.1	Synthesis of Isotropic Palladium Nanoparticles	306
9.2.1.1	Synthesis Using Polymer Stabilizers	307
9.2.1.2	Synthesis Using Thiol Stabilizers	308
9.2.1.3	Synthesis Using Dendrimer Stabilizers	310
9.2.1.4	Synthesis Using Thioether Stabilizers	311
9.2.1.5	Synthesis Using Phosphine and Bisphosphine Stabilizers	311
9.2.1.6	Synthesis Using DNA Stabilizers	314
9.2.2	Anisotropic Palladium Nanoparticles	314
9.2.2.1	Nanocubes, Nanorods and Nanocages	315
9.2.2.2	Triangular and Hexagonal Nanoplates	318
9.2.2.3	High-Aspect Ratio Pd Nanoparticles	322
9.2.3	Characterization	329
9.2.3.1	Electron Microscopy	329
9.2.3.2	Spectroscopic Techniques	333
9.2.3.3	Chemical Analysis Techniques	336
9.2.3.4	Physical Analysis Techniques	338
9.2.3.5	Electrochemistry	341
9.3	Life Sciences-Related Applications of Palladium Nanoparticles	343
9.3.1	Catalysis	343

9.3.1.1	Suzuki Reaction	346
9.3.1.2	Heck Reaction	347
9.3.1.3	Stille Reaction	347
9.3.1.4	Hydrogenation Reactions	347
9.3.2	Environmental Remediation	348
9.3.3	Sensing	348
9.4	Future Perspectives	349
	References	349
<b>10</b>	<b>Approaches to the Synthesis and Characterization of Spherical and Anisotropic Platinum Nanomaterials</b>	<b>357</b>
	<i>Zhenmeng Peng, Shengchun Yang and Hong Yang</i>	
10.1	Introduction	357
10.2	The Principles of Shape Control of Nanocrystals During Nucleation and Growth	359
10.2.1	Nucleation	359
10.2.1.1	Classical Nucleation Theory	359
10.2.1.2	Controllable Parameters for Nucleation	361
10.2.1.3	Types of Nucleation	362
10.2.2	Growth	363
10.2.2.1	Uniformity Control Related to the Morphology of Nanocrystals	363
10.2.2.2	Shape Controls	365
10.3	General Synthetic Approaches	370
10.3.1	Aqueous-Phase Synthesis	370
10.3.1.1	Colloidal Synthesis	370
10.3.1.2	Electrochemical Methods	373
10.3.1.3	Other Methods	373
10.3.2	Nonhydrolytic Synthesis	373
10.3.2.1	Solvents	375
10.3.2.2	Precursors	375
10.3.2.3	Reducing Agents	376
10.3.2.4	Capping Agents	376
10.4	Pseudo-Zero-Dimensional Pt Nanoparticles	376
10.4.1	Faceted Particles	377
10.4.1.1	Nanocubes	377
10.4.1.2	Tetrahedron, Cubo-Octahedral and Octahedron	378
10.4.1.3	Tetrahexahedron	379
10.4.2	Spherical Nanoparticles	379
10.5	One-Dimensional Nanostructures: Nanowires and Nanotubes	380
10.5.1	Nanowires	380
10.5.1.1	Polyol and Template-Free Synthesis	380
10.5.1.2	Template Synthesis	382
10.5.2	Nanotubes	383
10.6	Two-Dimensional Platinum Nanostructures	383
10.6.1	Planar Tripods and Bipods	384

10.6.2	Nanoplates	384
10.6.3	2-D Nanodendrites and Nanosheets	385
10.6.4	Porous Nanonetwork Prepared with the Langmuir–Blodgett (LB) Technique	385
10.7	Three-Dimensional Nanostructures	386
10.7.1	Pt Multipods and Flower-Like Nanostructures	386
10.7.1.1	Pt Multipods	386
10.7.1.2	Nanoflowers and Dendritic Nanostructures	387
10.7.2	Hollow Nanostructures	388
10.7.3	3-D Networks	389
10.8	Platinum Alloys and Intermetallics	390
10.9	Concluding Remarks	390
	Acknowledgments	391
	References	392

### **Part Three An Overview of Metallic Nanomaterials 403**

11	<b>Approaches to the Synthesis and Characterization of Spherical and Anisotropic Noble Metal Nanomaterials</b>	405
	<i>Harshala J. Parab, Hao Ming Chen, Nitin C. Bagkar, Ru-Shi Liu, Yeu-Kuang Hwu and Din Ping Tsai</i>	
11.1	General Introduction	405
11.1.1	Noble Metal Nanoparticles	407
11.1.2	Origin of Surface Plasmon Resonance in Noble Metal Nanoparticles	408
11.2	General Synthetic Strategies	410
11.2.1	Shape Variation	411
11.2.2	Nucleation and Growth	413
11.2.3	Chemical Synthetic Approach	414
11.2.3.1	Citrate Reduction	415
11.2.3.2	Polyol Synthesis	416
11.2.3.3	Seed-Mediated Synthesis	426
11.2.3.4	Other Methods	436
11.2.4	Bio-Based Synthetic Approach	437
11.2.4.1	Bacteria	437
11.2.4.2	Plants	440
11.2.4.3	Fungi	440
11.2.4.4	Actinomycetes, Yeast and Algae	441
11.3	Characterization of Anisotropic Nanostructures	441
11.3.1	Plasmonic Measurements of Single Gold Nanorod	442
11.3.2	XANES Analysis of Gold Nanoparticles	443
11.3.3	Theoretical Simulation of XANES	446
11.4	Conclusions and Future Perspectives	449
	Acknowledgments	449
	References	449

<b>12</b>	<b>Biological and Biomaterials-Assisted Synthesis of Precious Metal Nanoparticles</b>	<b>461</b>
	<i>Jason G. Parsons, Jose R. Peralta-Videa, Kenneth M. Dokken and Jorge L. Gardea-Torresdey</i>	
12.1	Introduction	461
12.2	Growth Process of Precious Metal Nanoparticles: Gold as an Example	463
12.3	Characterization Techniques for Nanomaterials Synthesized Through Biological Means	465
12.4	Morphology of Biologically Synthesized Precious Metal Nanoparticles	471
12.5	Inactivated Biological Tissues and Extracts for Nanoparticle Synthesis	473
12.5.1	Synthesis Using Inactivated Biological Tissues	473
12.5.1.1	Algal Biomass	474
12.5.1.2	Alfalfa Biomass	474
12.5.1.3	Oat and Wheat Biomasses	475
12.5.1.4	Hops Biomass	475
12.5.1.5	<i>Cinnamomum camphora</i> Biomass	476
12.5.2	Synthesis Using Extracts from Biological Tissues	476
12.6	Nanoparticle Synthesis Using Fungi and Bacteria	478
12.6.1	Fungal Synthesis of Precious Metal Nanoparticles	478
12.6.2	Bacterial Synthesis of Precious Metal Nanoparticles	480
12.7	Nanoparticle Synthesis by Living Plants	482
12.8	Conclusions	484
	Acknowledgments	484
	References	485
<b>13</b>	<b>Spherical and Anisotropic Gold Nanomaterials in Plasmonic Laser Phototherapy of Cancer</b>	<b>493</b>
	<i>Adela Ben-Yakar, Daniel Eversole and Ozgur Ekici</i>	
13.1	Introduction	493
13.2	Theoretical Understanding of Plasmonic Resonance	495
13.2.1	Origin of Surface Plasmon Resonance	495
13.2.2	Description of Absorption and Scattering Properties	496
13.2.3	Near-Field Scattering Dynamics	498
13.2.4	Tunable Optical Properties of Particles	500
13.2.4.1	Effect of Particle Aggregation	500
13.2.4.2	Effect of Particle Material Composition	501
13.2.4.3	Effect of Particle Geometric Changes	502
13.2.4.4	Near-Field Tunability	502
13.2.5	Plasmonic Summary	504
13.3	Understanding Nanoparticle Heating Properties	504
13.3.1	Fundamentals of Laser Heating of Nanoparticles and Their Surrounding Medium	504

13.3.2	Particle Heating/Cooling Models	506
13.3.2.1	Thermodynamic Model	506
13.3.2.2	Heat Transfer Model	506
13.3.3	Laser-Induced Phase Changes	509
13.3.4	Summary of Heating Dynamics	512
13.4	Plasmonic Laser Phototherapy (PLP)	513
13.4.1	Continuous-Wave Laser Plasmonic Phototherapy	514
13.4.1.1	In Vitro Cell Studies	514
13.4.1.2	In Vivo Animal Studies	517
13.4.2	Pulsed Laser Plasmonic Phototherapy	518
13.4.2.1	Localized Thermal Damage (Hyperthermia)	518
13.4.2.2	Bubble Formation	523
13.4.2.3	Overlapping Bubble Formation	525
13.4.2.4	Fragmentation of Nanoparticles	525
13.4.2.5	Nonlinear Absorption-Induced PLP	526
13.4.2.6	Plasmonic Laser Nanosurgery	527
13.4.3	Summary of Plasmonic Laser Phototherapy	528
13.5	Summary	529
13.6	Future Perspectives	530
	Acknowledgments	533
	References	533
<b>14</b>	<b>Application of Metallic Nanoparticles in Textiles</b>	<b>541</b>
	<i>Nadanathangam Vigneshwaran, Perianambi V. Varadarajan and Rudrapatna H. Balasubramanya</i>	
14.1	Introduction	541
14.2	Metal Nanomaterials	542
14.3	Nanotechnology in Textiles	543
14.3.1	Textile Finishing Processes	543
14.3.2	Textile Finishing Using Silver Nanoparticles	545
14.3.3	Textile Finishing Using Other Metal Nanoparticles	548
14.3.4	Metallic Versus Nonmetallic Nanoparticles in Textiles	551
14.4	Commercial Use of Nanotechnology in Textiles	552
14.5	Environmental Concerns	554
14.6	Conclusions	555
	References	555
	<b>Index</b>	<b>559</b>

