

Contents

Preface xv

1	Introduction to Upconversion and Upconverting Nanoparticles	1
	<i>Manisha Mondal and Vineet Kumar Rai</i>	
1.1	Introduction	1
1.2	Frequency Conversion and Its Various Processes	2
1.2.1	Stokes Emission	2
1.2.2	Anti-Stokes Emission	2
1.2.2.1	Ground/Excited-State Absorption (GSA/ESA)	3
1.2.2.2	Energy Transfer Upconversion (ETU)	4
1.2.2.3	Cooperative Luminescence and Cooperative Sensitization Upconversion (CSU)	5
1.2.2.4	Cross-relaxation (CR) and Photon Avalanche (PA)	6
1.3	Transition Metals and Their Properties	7
1.4	Rare Earths and Their Properties	8
1.4.1	Trivalent Rare-Earth Ions	9
1.4.1.1	Electronic Structure	9
1.4.1.2	Interaction of Rare-Earth Ions	10
1.4.1.3	Dieke Diagram	13
1.4.2	Divalent Rare-Earth Ions	13
1.5	Excitation and De-excitation Processes of Rare Earths in Solid Materials	15
1.5.1	Excitation Processes	15
1.5.1.1	f-f Transition	15
1.5.1.2	f-d Transition	15
1.5.1.3	Charge Transfer Transition	15
1.5.2	Emission Processes	15
1.5.2.1	Emission via Radiative Transitions	15
1.5.2.2	Emission via Nonradiative Transitions	16
1.5.2.3	Energy Transfer Processes	16
1.6	Rate Equations Relevant to UC Mechanism	18
1.6.1	Rate Equations in a Basic Three-Level System	18

1.6.2	Rate Equation Related to Pump Power-Dependent UC Emission	19
1.7	Theoretical Description of Optical Characteristics of Rare-Earth Ions	20
1.7.1	Judd–Ofelt (J–O) Theory and Calculation of Radiative Parameters	21
1.7.2	Nephelauxetic Effect	22
1.8	An Introduction to Upconverting Nanoparticles	22
	Acknowledgments	23
	References	23
2	Synthesis Protocol of Upconversion Nanoparticles	31
	<i>Lakshmi Mukhopadhyay and Vineet Kumar Rai</i>	
2.1	Introduction	31
2.2	Host Matrix	32
2.3	Synthetic Strategy of UC Nanomaterials	33
2.3.1	Solid-State Reaction Technique	34
2.3.2	Coprecipitation Technique	35
2.3.3	Sol–Gel Technique	36
2.3.4	Hydro(solvo)thermal Technique	39
2.3.5	Combustion Technique	40
2.3.6	Thermolysis Technique	42
2.3.6.1	Thermolysis in OA-Based Mixed Solvents	43
2.3.6.2	Thermolysis in OM-Based Mixed Solvents	43
2.3.6.3	Thermolysis in TOPO-Based Mixed Solvents	43
2.3.7	Microwave-Assisted Synthesis Technique	44
2.4	Synthesis Techniques for Fabricating Core@shell Architectures	45
2.4.1	Solid-Phase Reaction	45
2.4.2	Liquid-Phase Reaction	46
2.4.2.1	Stöber Technique	46
2.4.2.2	Microemulsion Technique	48
2.4.3	Gas-Phase Reaction	51
2.4.4	Mechanical Mixing	52
2.5	Other Synthesis Strategies to Develop Lanthanide-Doped UCNPs	52
2.6	Conclusion	53
	References	53
3	Characterization Techniques and Analysis	67
	<i>Neha Jain, Prince K. Jain, Rajan K. Singh, Amit Srivastava, and Jai Singh</i>	
3.1	Introduction	67
3.2	X-Ray Diffraction (XRD)	69
3.3	X-ray Photoelectron Spectroscopy (XPS)	72
3.4	Field Emission Scanning Electron Microscopy (FESEM)	74
3.5	Transmission Electron Microscopy (TEM)	76
3.6	Energy-Dispersive X-ray Spectroscopy (EDS)	79
3.7	Thermogravimetric Analysis (TGA)	81
3.8	Ultraviolet–Visible–Near-Infrared (UV–Vis–NIR) Absorption Spectroscopy	82

- 3.9 Dynamic Light Scattering (DLS) 84
- 3.10 Photoluminescence (PL) Study 85
- 3.11 Pump Power-Dependent UC 87
- 3.12 Recognition of Emission Color and Colorimetric Theory 88
- Acknowledgment 89
- References 89

- 4 Raman and FTIR Spectroscopic Techniques and Their Applications 97**
Saurav K. Ojha and Animesh K. Ojha
- 4.1 Raman Spectroscopy 97
- 4.2 Fourier Transform Infrared (FTIR) Spectroscopy 99
 - 4.2.1 FTIR in Transmission Mode 100
 - 4.2.2 Attenuated Total Reflectance (ATR) 100
 - 4.2.3 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) 100
- 4.3 Applications of Raman Spectroscopy 100
 - 4.3.1 Raman Study of Molecular Association in Hydrogen-Bonded Systems 100
 - 4.3.2 Surface-Enhanced Raman Spectroscopy (SERS) 104
 - 4.3.3 Resonance Raman Spectroscopy (RRS) 106
 - 4.3.4 Raman Spectroscopy of Semiconducting, Superconducting, and Perovskite Materials 107
- 4.4 Applications of FTIR Spectroscopy 108
 - 4.4.1 FTIR Spectroscopy of Semiconductor, Superconductor, Hazardous, and Perovskite Materials 108
- 4.5 Raman and FTIR Spectroscopy of Upconverting Nanoparticles 109
- References 110

- 5 Fundamental Aspects of Upconverting Nanoparticles (UCNPs) Based on Their Properties 117**
Sushil K. Ranjan, Sasank Pattnaik, Vishab Kesarwani, and Vineet Kumar Rai
- 5.1 Introduction 117
- 5.2 Elucidation of Dynamics of UCNPs on the Basis of Fluorescence Decay Times 120
 - 5.2.1 General Understanding of Depopulation Processes and UC Decay 120
 - 5.2.2 Differentiating the ESA and ETU Mechanism Based on the Decay Profile 121
 - 5.2.3 Theoretical and Experimental Approach of Understanding the Factors Affecting Upconversion Decay 123
- 5.3 Measurement of Quantum Yield of UCNPs 131
 - 5.3.1 Role of Quantum Yield in Upconversion 132
 - 5.3.2 Optical Methods of Measuring Quantum Yield of Upconverting Nanoparticles (UCNPs) 133
 - 5.3.2.1 Relative Method of Measuring Quantum Yield 133

- 5.3.2.2 Absolute Method of Measuring Quantum Yield 133
- 5.3.2.3 Measurement of Intrinsic Quantum Yield of Lanthanide-Based Materials Using Lifetimes 134
- 5.3.3 Some Other Methods of Determining Quantum Yield 134
- 5.3.3.1 Photo-acoustic Spectroscopy (PAS) 134
- 5.3.3.2 Thermal Lensing (TL) Method 135
- References 135

6 Frequency Upconversion in UCNPs Containing Transition Metal Ions 141

Manisha Prasad and Vineet Kumar Rai

- 6.1 Introduction 141
- 6.2 Synthesis of Transition Metal Ion-Activated Luminescent Nanomaterials 143
- 6.3 Structural and Optical Characterizations 143
- 6.4 Frequency Upconversion and Its Various Mechanisms 144
- 6.5 Applications 144
- 6.6 Mechanism of Transition Metal Ions in Crystal Field 145
- 6.6.1 UC Mechanisms in Mn-Based System 146
- 6.6.2 UC Mechanisms in Mn⁴⁺- and Ti²⁺-Based Systems 151
- 6.6.3 UC Mechanisms in Cr³⁺-Based System 153
- 6.6.4 UC Mechanisms in the Fe³⁺-Based System 155
- 6.6.5 UC Mechanisms in Co³⁺- and Ni²⁺-Based System 157
- 6.6.6 UC Mechanisms in Cu²⁺-, Zn²⁺-, and Zr⁴⁺-Based System 158
- 6.6.7 UC Mechanisms in Nb⁵⁺-, Mo³⁺-, Ru-, and Ag⁺-Based System 160
- 6.6.8 UC Mechanisms in W⁶⁺- and Re⁴⁺-Based System 161
- 6.6.9 UC Mechanisms in Os⁴⁺- and Au-Based System 162
- References 164

7 Frequency Upconversion in UCNPs Containing Rare-Earth Ions 171

Sasank Pattnaik and Vineet Kumar Rai

- 7.1 Introduction 171
- 7.2 Familiarization with the Spectroscopic Behavior of RE³⁺ Ion-Doped UCNPs 173
- 7.2.1 Physics of Trivalent Rare-Earth Ions 173
- 7.2.1.1 UC Mechanisms in Yb³⁺- and Pr³⁺-Based Systems 174
- 7.2.1.2 UC Mechanisms in Er-Based Systems 175
- 7.2.1.3 UC Mechanisms in Ho-Based Systems 177
- 7.2.1.4 UC Mechanisms in Tm-Based Systems 179
- 7.2.1.5 UC Mechanisms in Nd-Based Systems 181
- 7.2.1.6 Tri-Doped Systems 181
- 7.2.2 Color Modulation in UCNPs 184
- 7.2.2.1 Role of Dopant Concentration and Combination of RE³⁺ Ions in Color Modulation 184

7.2.2.2	Role of Host/Dopant Combination in Color Modulation	186
7.2.2.3	Controlling the Emission Color Through Phonon Effects	186
7.2.2.4	Tuning UC Emission Using FRET	188
7.2.3	Quenching Mechanisms in UCNPs	190
7.3	Routes to Enhance Upconversion Luminescence in Nanoparticles	190
7.3.1	Dye Sensitization Techniques	191
7.3.2	Concentration Quenching Minimization	192
7.3.2.1	Suppression of Surface-Related Quenching	192
7.3.2.2	Removal of Detrimental Cross-Relaxation	193
7.3.3	Confinement of Energy Migration	194
7.3.4	Other Techniques to Enhance Upconversion Emission	195
7.3.4.1	Crystal-Phase Modification	195
7.3.4.2	Constructing an Active Core/Active Shell Strategy	195
7.3.4.3	Conjugating Surface Plasmon Resonance Technique	195
7.3.4.4	Dielectric Superlensing-Mediated Strategy	196
7.4	Technological Applications	197
7.4.1	Photonic Applications	197
7.4.1.1	Light-Emitting Diodes (LEDs)	197
7.4.1.2	Photovoltaic Applications	198
7.4.2	Bioimaging	199
7.4.3	Photo-Induced Therapeutic Applications	200
7.4.3.1	Photodynamic Therapy	201
7.4.3.2	Photothermal Therapy	201
7.4.3.3	Photoactivated Chemotherapy (PACT)	202
7.4.4	Other Emerging Applications	203
7.4.4.1	Anticounterfeiting	203
7.4.4.2	Sensing and Detection	203
7.4.4.3	Optogenetic Stimulation	205
7.4.4.4	NIR Image Vision of Mammals	205
	References	206

8 Smart Upconverting Nanoparticles and New Types of Upconverting Nanoparticles 221

Akhilesh K. Singh

8.1	Introduction	221
8.2	Upconverting Core–Shell Nanostructures	222
8.3	Hybrid Upconverting Nanoparticles	224
8.4	Magnetic Upconverting Nanoparticles	226
8.5	UC-Based Metal–Organic Frameworks	228
8.6	Smart UCNPs for Security Applications	230
8.7	Smart Upconverting Nanoparticles for Biological Applications	233
8.8	Smart Upconverting Nanoparticles for Sensing	235
8.9	Conclusion	236
	References	237

9	Surface Modification and (Bio)Functionalization of Upconverting Nanoparticles 241
	<i>Yashashchandra Dwivedi</i>
9.1	Introduction 241
9.2	Upconverting Nanomaterials 242
9.3	Surface Modification 245
9.4	Biofunctionalization of Upconverting Materials and Applications 247
	References 257
10	Frequency Upconversion in Core@shell Nanoparticles 267
	<i>Raghumani S. Ningthoujam, Rashmi Joshi, and Manas Srivastava</i>
10.1	Introduction 267
10.1.1	Downconversion 267
10.1.2	Upconversion 271
10.2	Synthesis of Core@shell and Core@shell@shell UCNPs 272
10.2.1	Thermolysis Method 272
10.2.2	Hot Injection 276
10.2.3	Cation Exchange 277
10.2.4	Structural Characterizations 277
10.2.5	Optical Characterization 281
10.2.5.1	Normal Conversion Process in Ln-Doped Core@shell Nanoparticles 283
10.2.5.2	Loop-Type and Avalanche-Type Upconversion Processes in Core@shell Nanoparticles 289
10.3	Frequency Upconversion and Its Various Mechanisms 291
10.3.1	Inorganic-Based Upconversion 291
10.4	Applications 297
10.4.1	Bioimaging Applications 297
10.4.1.1	Luminescence-Based Imaging 297
10.4.1.2	Other Imaging Probes (MRI, CT, and SPECT) 299
10.4.2	Photothermal Therapy (PTT) 301
10.4.3	Photodynamic Therapy (PDT) 303
10.4.4	Temperature Sensor 306
10.4.5	Security Ink 308
10.5	Conclusion 310
	Acknowledgment 311
	References 311
11	UCNPs in Solar, Forensic, Security Ink, and Anti-counterfeiting Applications 319
	<i>Kaushal Kumar, Neeraj Kumar Mishra, and Kumar Shwetabh</i>
11.1	Introduction 319
11.2	UCNPs for Solar Cells 320
11.2.1	C-Si Solar Cells 321

11.2.2	Amorphous Silicon Solar Cells	323
11.2.3	GaAs-Based Solar Cells	324
11.2.4	Dye-Sensitized Solar Cells (DSSCs)	324
11.3	Forensic, Security Printing, and Anti-counterfeiting Applications	325
11.4	Biomedicals	331
11.4.1	Bioimaging	333
11.4.2	Biosensing	336
11.5	Display and Lighting Purposes	339
	References	340
12	Application of Upconversion in Photocatalysis and Photodetectors	347
	<i>Priyam Singh, Sachin Singh, and Prabhakar Singh</i>	
	<i>Sunil Kumar Singh</i>	
12.1	Introduction	347
12.2	Photocatalysis	349
12.3	Photodetector	357
12.4	Conclusion	365
	References	365
13	UCNPs in Lighting and Displays	375
	<i>Riya Dey</i>	
13.1	Introduction	375
13.2	Major Factors that Affect the UC Emission Efficiency	375
13.3	UC Mechanisms with Rate Equations	378
13.3.1	Pump Power Dependence in the Case of Dominant ETU-Assisted Upconversion over ESA	379
13.3.2	Pump Power Dependence in the Case of Dominant ESA-Assisted Upconversion over ETU	380
13.4	UCNPs in Solid-State Laser	380
13.5	UCNPs in Solid-State Lighting and Displays	384
13.5.1	Requirements for LED Applications	384
	References	388
14	Upconversion Nanoparticles in pH Sensing Applications	395
	<i>Manoj Kumar Mahata, Ranjit De, and Kang Taek Lee</i>	
14.1	Introduction	395
14.2	Basic Properties of UCNPs	397
14.3	Working Principle of UCNP-Based pH Sensor	400
14.4	Photon Upconversion-Based pH Sensing Systems	401
14.4.1	Upconversion Nanoparticles as pH Sensors	401
14.4.2	Upconversion-Based pH Sensing Membranes	405
14.5	Conclusion	410
	References	411

- 15 Upconversion Nanoparticles in Temperature Sensing and Optical Heating Applications 417**
Praveen K. Shahi and Shyam B. Rai
- 15.1 Introduction 417
 - 15.2 Classification of Temperature Sensors: Primary and Secondary Thermometers 420
 - 15.3 Performance of Temperature Sensors 420
 - 15.3.1 Thermal Sensitivity 421
 - 15.3.2 Thermal Uncertainty (δT) 421
 - 15.3.3 Reproducibility and Repeatability 422
 - 15.4 Temperature Sensing with Luminescence 423
 - 15.4.1 Time-Integrated Schemes 424
 - 15.4.1.1 Fluorescence Intensity Ratio (FIR) or Band Shape 424
 - 15.4.1.2 Bandwidth 426
 - 15.4.2 Lifetime Technique 427
 - 15.5 Upconversion (UC) and UC-Based Thermal Sensor of Ln^{3+} Ions 427
 - 15.5.1 Upconversion (UC) and Upconverting Nanoparticles (UCNPs) 427
 - 15.5.2 Single-Center UC Nanothermometers and Multicenter UC Nanothermometers 428
 - 15.5.3 Complex Systems 430
 - 15.6 Optical Heating 433
 - References 437
- 16 Upconverting Nanoparticles in Pollutant Degradation and Hydrogen Generation 449**
Wanni Wang, Zhaoyou Chu, Benjin Chen, and Haisheng Qian
- 16.1 Introduction 449
 - 16.2 Degradation of Organic Pollutants 450
 - 16.2.1 Degradation of RhB 451
 - 16.2.2 Degradation of MB 455
 - 16.2.3 Degradation of MO 460
 - 16.2.4 Degradation of Various Organic Pollutants 462
 - 16.2.5 Others 467
 - 16.3 Degradation of Inorganic Pollutants 469
 - 16.4 Photocatalytic Hydrogen Production 473
 - 16.5 Conclusion 481
 - References 481
- 17 Upconverting Nanoparticles in the Detection of Fungicides and Plant Viruses 493**
Vishab Kesarwani and Vineet Kumar Rai
- 17.1 Introduction 493
 - 17.2 Visual Detection of Fungicides 495
 - 17.2.1 Detection Mechanisms 495
 - 17.2.1.1 Forster Resonance Energy Transfer (FRET) 495

17.2.1.2	Inner Filter Effect (IFE)	496
17.2.1.3	Photoinduced Electron Transfer (PET)	499
17.2.1.4	Electron Exchange (EE)	500
17.2.2	Significant Works on Upconversion-Based Fungicide Detection	500
17.3	Detection of Plant Viruses	505
17.3.1	Plant Virus Detection/Management Strategies	505
17.3.1.1	Direct Interactions	505
17.3.1.2	Indirect Interactions	505
17.3.1.3	NPs as Biosensors for Virus Detection	507
17.3.1.4	RNAi Process for Antiviral Protection	507
17.3.2	Significant Works on Plant Virus Detection Based on UCNPs	507
17.4	Future Challenges Regarding NP-Based Fungicide and Plant Virus Detection	509
	References	510
18	Upconversion Nanoparticles in Biological Applications	517
	<i>Poulami Mukherjee and Sumanta Kumar Sahu</i>	
18.1	Introduction	517
18.2	Upconversion Nanoparticles in Bioimaging	518
18.2.1	Cell Imaging	518
18.2.2	Multimodal Imaging	520
18.3	Upconversion Nanoparticles in Drug Delivery	522
18.3.1	Different Types of Surface Modification	524
18.3.1.1	Polymer Coating	524
18.3.1.2	Silica Coating	524
18.3.1.3	Metal Oxide-Coated UCNPs	525
18.3.1.4	Functionalization of UCNPs	525
18.3.1.5	Metal–Organic Framework Coating	525
18.3.2	Drug Release	526
18.3.2.1	NIR-Triggered Drug Delivery System	526
18.3.2.2	pH and Thermoresponsive Drug Release	526
18.4	Upconversion in Photodynamic Therapy	526
18.4.1	Surface Modification of UCNPs for PDT	529
18.5	Photothermal Therapy	531
	References	533
	Index	539

