

Contents

Preface *xiii*

Acknowledgments *xv*

- 1 Introduction to Nanocellulose** *1*
Jin Huang, Xiaozhou Ma, Guang Yang, and Dufresne Alain
- 1.1 Introduction *1*
 - 1.2 Preparation of Nanocellulose *2*
 - 1.2.1 Cellulose Nanocrystals *2*
 - 1.2.2 Cellulose Nanofibers *3*
 - 1.2.3 Bacterial Nanocellulose *4*
 - 1.3 Surface Modification of Nanocellulose *4*
 - 1.3.1 Esterification *7*
 - 1.3.2 Oxidation *7*
 - 1.3.3 Etherification *8*
 - 1.3.4 Amidation *8*
 - 1.3.5 Other Chemical Methods *8*
 - 1.3.6 Physical Interaction *9*
 - 1.4 Nanocellulose-Based Materials and Applications *9*
 - 1.5 Conclusions and Prospects *13*
 - References *15*
- 2 Structure and Properties of Cellulose Nanocrystals** *21*
Chunyu Chang, Junjun Hou, Peter R. Chang, and Jin Huang
- 2.1 Introduction *21*
 - 2.2 Extraction of Cellulose Nanocrystals *21*
 - 2.2.1 Extraction of Cellulose Nanocrystals by Acid Hydrolysis *21*
 - 2.2.2 Pretreatments of Cellulose Before Acid Hydrolysis *27*
 - 2.2.3 Other Methods of Preparing Cellulose Nanocrystals *31*
 - 2.3 Structures and Properties of Cellulose Nanocrystals *32*
 - 2.3.1 Physical Properties of Cellulose Nanocrystals *32*
 - 2.3.2 Properties of Cellulose Nanocrystal Suspension *39*
 - References *45*

3	Structure and Properties of Cellulose Nanofibrils	53
	<i>Pei Huang, Dayong Huang, Yong Huang, and Min Wu</i>	
3.1	Production of CNF	53
3.1.1	Chemical Bleaching	54
3.1.2	Mechanical Disintegration	54
3.1.2.1	Homogenization	54
3.1.2.2	Grinding	58
3.1.2.3	Ball-milling	59
3.1.2.4	Ultrasonication	59
3.1.2.5	Steam Explosion	61
3.1.2.6	Aqueous Counter Collision	61
3.1.2.7	Refining	62
3.1.2.8	Cryocrushing	62
3.1.2.9	Twin-Screw Extrusion	62
3.1.2.10	Other Methods	63
3.1.3	Pretreatment	63
3.2	Features and Properties	64
3.2.1	Morphology and Size of CNF	64
3.2.2	Crystallization of CNF	65
3.2.3	Processing and Products	65
3.3	Conclusion	73
	References	73
4	Synthesis, Structure, and Properties of Bacterial Cellulose	81
	<i>Muhammad Wajid Ullah, Sehrish Manan, Sabella J. Kiprono, Mazhar Ul-Islam, and Guang Yang</i>	
4.1	Introduction	81
4.2	Biogenesis of Bacterial Cellulose	83
4.2.1	Biochemistry of BC Synthesis	83
4.2.2	Biochemical Pathway of BC Production	85
4.2.3	Molecular Regulation of BC Synthesis	87
4.3	Structure and Exciting Features of Bacterial Cellulose	88
4.3.1	Chemical Structure and Properties	89
4.3.2	Physiological Features	89
4.3.3	Self-assembly and Crystallization	90
4.3.4	Ultrafine Thin Fibrous Structure	90
4.3.5	Macrostructure Control and Orientation	91
4.3.6	Porosity and Materials Absorption Potential of BC for Composite Synthesis	91
4.3.7	Biocompatibility	92
4.3.8	Biodegradability	92
4.4	Production of Bacterial Cellulose: Synthesis Approaches	93
4.4.1	Static Fermentative Cultivation: Production of BC Membrane, Film, or Sheet	93
4.4.2	Shaking Fermentative Cultivation: Production of BC Pellets	94
4.4.3	Agitation Fermentative Cultivation: Production of BC Granules	94
4.4.3.1	Rotating Disk Reactor	95

4.4.3.2	Trickling Bed Reactor	95
4.5	Additives to Enhance BC Production	95
4.5.1	Carboxymethylcellulose	97
4.5.2	Organic Acids	97
4.5.3	Vitamin C	97
4.5.4	Sodium Alginate	99
4.5.5	Alcohols	99
4.5.6	SSGO	99
4.5.7	Lignosulfate	100
4.5.8	Agar and Xanthan	100
4.5.9	Thin Stillage	100
4.6	Strategies Toward Low-Cost BC Production	101
4.6.1	Fruit Juices	101
4.6.2	Sugarcane Molasses	101
4.6.3	Agricultural and Industrial Wastes	103
4.6.4	Food Wastes	104
4.7	Conclusions and Future Prospects	105
	Acknowledgment	105
	References	106
5	Surface Chemistry of Nanocellulose	115
	<i>Ge Zhu and Ning Lin</i>	
5.1	Brief Introduction to Nanocellulose Family	115
5.1.1	Cellulose Nanocrystals (CNCs)	115
5.1.2	Cellulose Nanofibrils (CNFs)	117
5.1.3	Bacterial Cellulose (BC)	117
5.2	Surface Modification of Nanocellulose	119
5.2.1	Physical Adsorption of Surfactants	119
5.2.2	Sulfonation	121
5.2.3	TEMPO-oxidation	122
5.2.4	Esterification	123
5.2.5	Silylation	125
5.2.6	Grafting Onto	126
5.2.7	Grafting From	131
5.2.7.1	Ring-Opening Polymerization (ROP)	132
5.2.7.2	Living Radical Polymerization (LRP)	134
5.2.8	Chemical Modification from End Hemiacetal	137
5.3	Advanced Functional Modifications	139
5.3.1	Fluorescent and Dye Molecules	139
5.3.2	Amino Acid and DNA	142
5.3.3	Self-cross-linking of Nanocrystals	144
	References	145
6	Current Status of Nanocellulose-Based Nanocomposites	155
	<i>Xiaozhou Ma, Yuhuan Wang, Yang Shen, Jin Huang, and Alain Dufresne</i>	
6.1	Introduction	155
6.2	Cellulose Nanocrystal-Filled Nanocomposites	156

6.2.1	Polyolefin-Based Nanocomposites	156
6.2.2	Rubber-Based Nanocomposites	161
6.2.3	Polyester-Based Nanocomposites	164
6.2.4	Polyurethane- and Waterborne Polyurethane-Based Nanocomposites	167
6.2.5	Epoxy- and Waterborne Epoxy-Based Nanocomposites	169
6.2.6	Natural Polymer-Based Nanocomposites	171
6.3	Fibrillated Cellulose-Filled Nanocomposites	172
6.3.1	Polyolefin-Based Nanocomposites	172
6.3.2	Rubber-Based Nanocomposites	176
6.3.3	Polyester-Based Nanocomposites	178
6.3.4	Polyurethane- and Waterborne Polyurethane-Based Nanocomposites	180
6.3.5	Natural Polymer-Based Nanocomposites	182
6.3.6	Other Polymer Nanocomposites Filled with Fibrillated Cellulose	184
6.4	Conclusion and Prospect	186
	References	186

7 Reinforcing Mechanism of Cellulose Nanocrystals in Nanocomposites 201

Yaoyao Chen, Lin Gan, Jin Huang, and Alain Dufresne

7.1	Percolation Approach	201
7.1.1	Mean-Field Theory	202
7.1.2	Percolation Model	204
7.1.3	Factors Influencing the Percolation Network Formation	208
7.2	Interfacial Behaviors Between Cellulose Nanocrystals and Matrix	211
7.2.1	Effect of Functional Groups on CNC Surface on Interfacial Interaction	211
7.2.2	Effect of Segmental Entanglement Mediated with Grafted Chains on CNC Surface	225
7.2.3	Role of Co-continuous Structure Derived from Chemical Coupling of Filler/Matrix	229
7.2.3.1	Thiol-ene Coupling Process Between Modified Cellulose Nanocrystals (CNCs) and Matrix	230
7.2.3.2	Huisgen Cycloaddition Click Chemistry Between Modified CNCs and Matrices	232
7.2.3.3	Schiff's Base Reaction Between Cellulose Nanocrystals (CNCs) and Matrix	233
7.2.3.4	Esterification Reaction Between CNCs and The Matrix	237
7.2.3.5	Chemical Coupling Between Hydroxyl Groups of Matrix and Aldehyded CNCs or Modified CNCs	237
7.3	Conclusions	242
	References	243

8	Role of Cellulose Nanofibrils in Polymer Nanocomposites	251
	<i>Thiago H. S. Maia, Marília Calazans, Vitor Lima, Francys K. V. Moreira, and Alessandra de Almeida Lucas</i>	
8.1	Introduction	251
8.2	Characteristics of Cellulose Nanofibrils	252
8.3	Mechanical Properties of CNF Polymer Nanocomposites	253
8.3.1	Thermoset Resins	254
8.3.2	Thermoplastics	255
8.3.3	Waterborne Polymer Systems	257
8.4	Effects of Extrusion on Mechanical Properties of PE/CNF Nanocomposites	258
8.5	Effect of Fiber Size and Lignin Presence	264
8.6	Multifunctionality: Optical and Barrier Properties of CNF Nanocomposites	267
8.7	Outlooks in CNF Nanocomposites	269
	References	269
9	Advanced Materials Based on Self-assembly of Cellulose Nanocrystals	277
	<i>Lin Gan, Siyuan Liu, Dong Li, and Jin Huang</i>	
9.1	Self-assembly Structure of CNCs	277
9.1.1	Structure of CNC Liquid Crystals	278
9.1.2	Components of CNC Self-assembly	279
9.1.3	Form of CNC Self-assembly Products	279
9.2	Self-assembly Methods and Materials	281
9.2.1	Casting Method and Spin Coating Method	281
9.2.2	Vacuum-Assisted Self-assembly	283
9.2.3	Evaporation-Induced Self-assembly	284
9.3	Structural Adjustment of CNC Self-assembly	284
9.3.1	Cholesteric Structure of Neat CNC Films	284
9.3.2	Cholesteric Structure and Cross-linking Structure in Gel	286
9.3.3	Cholesteric Structure in Bulk Materials of CNC Composite Self-assembly	288
9.3.4	Nematic Structure	290
9.4	Modifying Surface Chemical Structure of CNC	291
9.5	Properties of CNC Self-assembly	295
9.5.1	Mechanical Properties	295
9.5.1.1	Mechanical Properties of CNC Films	295
9.5.1.2	Mechanical Properties of CNC Composite Films	295
9.5.2	Iridescent Color	298
9.5.2.1	Iridescent Color Control of CNC Films	298
9.5.2.2	Iridescent Color Control of CNC Composite Materials	300
9.5.2.3	Optical Control of CNC Self-assembly Gels	302
9.5.3	Plasmonic Properties of CNC	304

- 9.6 Potential Applications 305
 - 9.6.1 Oil/Water Separation 305
 - 9.6.2 Application of Optical Materials 306
 - 9.6.2.1 Optical Application of CNC Films 306
 - 9.6.2.2 Optical Application of CNC Composite Films 306
 - 9.6.3 Sensors 307
- References 309

- 10 Potential Application Based on Colloidal Properties of Cellulose Nanocrystals 315**
Shiyu Fu and Linxin Zhong
 - 10.1 Colloidal Properties of CNC and Applications in Functional Materials 315
 - 10.2 Nanocellulose for Paper and Packaging 324
 - 10.2.1 Nanocellulose for Paper Coating 326
 - 10.2.2 Microfibrillated Cellulose Coated Paper for Delivery System 328
 - 10.2.3 Water-Resistant Nanopaper Based on Modified Nanocellulose 329
 - 10.2.4 Effect of Chemical Composition on Microfibrillar Cellulose Film 334
 - 10.2.5 Antimicrobial Diffusion Films Based on Microfibrillated Cellulose 336
 - 10.3 Nanocellulose for Wood Coatings 339
- References 341

- 11 Strategies to Explore Biomedical Application of Nanocellulose 349**
Yanjie Zhang, Peter R. Chang, Xiaozhou Ma, Ning Lin, and Jin Huang
 - 11.1 Introduction 349
 - 11.2 Research on Biological Toxicity of Nanocellulose 349
 - 11.3 Application of Nanocellulose for Immobilization and Recognition of Biological Macromolecules 355
 - 11.4 Application of Nanocellulose for Cell Imaging 360
 - 11.5 Application of Nanocellulose for Cell Scaffolds 361
 - 11.6 Application of Nanocellulose in Tissue Engineering 366
 - 11.6.1 Tissue Repairing, Regeneration, and Healing 366
 - 11.6.1.1 Skin Tissue Repairing 368
 - 11.6.1.2 Bone Tissue Regeneration 370
 - 11.6.2 Tissue Replacement 371
 - 11.6.2.1 Artificial Blood Vessels 371
 - 11.6.2.2 Soft Tissues, Meniscus, and Cartilage 373
 - 11.6.2.3 Nucleus Pulposus Replacement 375
 - 11.7 Application of Nanocellulose in Drug Carrier and Delivery 375
 - 11.8 Application of Nanocellulose as Biomedical Materials 382
 - 11.8.1 Antimicrobial Nanomaterials 382
 - 11.8.1.1 Nanocellulose Incorporated with Inorganic Antimicrobial Agents 385
 - 11.8.1.2 Nanocellulose Incorporated with Organic Antimicrobial Agents 386

- 11.8.2 Medical Composite Material 388
- 11.9 Summary 389
 - References 389

- 12 Application of Nanocellulose in Energy Materials and Devices 397**
 - Gang Chen and Zhiqiang Fang*
 - 12.1 Introduction 397
 - 12.2 Nanocellulose for Lithium Ion Batteries (LIBs) 398
 - 12.2.1 Nanocellulose-Based Electrodes 398
 - 12.2.2 Nanocellulose-Based Separators 401
 - 12.2.3 Nanocellulose-Based Electrolytes 403
 - 12.2.4 Nanocellulose-Based Binders 403
 - 12.3 Nanocellulose for Supercapacitors 404
 - 12.3.1 Nanocellulose As a Substrate 405
 - 12.3.2 Nanocellulose As a Nano-template 406
 - 12.3.3 Nanocellulose As a Mesoporous Membrane 410
 - 12.4 Nanocellulose for Other Energy Devices 411
 - 12.4.1 Fuel Cells 411
 - 12.4.2 Solar Cells 412
 - 12.4.3 Nanogenerators 414
 - 12.5 Conclusion and Outlook 415
 - References 416

- 13 Exploration of Other High-Value Applications of Nanocellulose 423**
 - Ruitao Cha, Xiaonan Hao, Kaiwen Mou, Keying Long, Juanjuan Li, and Xingyu Jiang*
 - 13.1 Fire Resistant Materials 423
 - 13.1.1 Introduction 423
 - 13.1.2 Flame Retardant Additives 424
 - 13.1.2.1 Halogenated Flame Retardants 424
 - 13.1.2.2 Phosphorus-Based Flame Retardants 424
 - 13.1.2.3 Nitrogen-Based Flame Retardants 424
 - 13.1.2.4 Silicon-Based Flame Retardants 424
 - 13.1.2.5 Mineral Flame Retardants 425
 - 13.1.2.6 Nanoparticles 425
 - 13.1.3 Fire Resistance of Clay Nanopaper Based on Nanocellulose 425
 - 13.1.4 Conclusion 432
 - 13.2 Thermal Insulation Materials 432
 - 13.2.1 Introduction 432
 - 13.2.2 Thermal Building Insulation Materials 432
 - 13.2.2.1 Mineral Wool 433
 - 13.2.2.2 Expanded Polystyrene (EPS) 433
 - 13.2.2.3 Polyurethane (PUR) 433
 - 13.2.2.4 Aerogel 433

13.2.3	Thermal Insulation Performance of Nanocellulose-Based Materials	434
13.2.4	Conclusion	437
13.3	The Templated Materials	438
13.3.1	Introduction	438
13.3.2	Synthesis of Magnetic Composite Aerogels	442
13.3.3	Synthesis of Inorganic Hollow Nanotube Aerogels	454
13.3.4	The Self-assembled CNC Templates	458
13.3.5	Conclusion	464
	References	464
	Index	475