## "十二五"国家重点图书

Advanced Functional Materials Series 先进功能材料丛书 丛书主编 师昌绪

# Polysaccharide-Based Nanocrystals

**Chemistry and Applications** 

# 聚多糖纳米晶——化学与应用

Edited by Jin Huang, Peter R. Chang, Ning Lin, and Alain Dufresne

黄 进 彼得·张荣贵 林 宁 阿兰·迪弗雷纳 编著





Advanced Functional Materials Series 先进功能材料丛书 丛书主编 师昌绪

# Polysaccharide-Based Nanocrystals

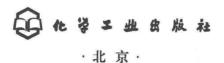
**Chemistry and Applications** 

聚多糖纳米晶——化学与应用

Edited by Jin Huang, Peter R. Chang, Ning Lin, and Alain Dufresne

黄 进 彼得·张荣贵 林 宁 阿兰·迪弗雷纳 编著

WILEY-VCH



本书采用简明的语言、丰富的数据图表,阐明了来自天然生物质资源的聚多糖纳米晶的提取、结构、性质、化学修饰、材料制备等方面的理论知识和实践经验,总结了聚多糖纳米晶改性材料功能化、高性能化的研究思路和技术方案。不仅包含作者在过去十年中以保护环境和降低石油消耗为目标,围绕可再生、可生物降解的聚多糖纳米晶发展成为高性能材料及功能材料的研究工作的凝练,同时涵盖了国内外同行的优秀研究成果。

本书主要包括纤维素纳米晶、甲壳素纳米晶及淀粉纳米晶的制备、化学和物理改性、纳米复合材料和功能材料构建的相关理论和技术等内容,并且对聚多糖纳米晶的理论研究体系建立、应用拓展及发展方向等进行了展望。

本书可供生物质化学与化工、高分子科学、环境科学、材料科学、农业化学、纳米科学与技术等相关专业的研究生学习使用,也可作为相关科研工作者和工程技术人员的参考书。

### 图书在版编目(CIP)数据

聚多糖纳米晶: 化学与应用 = Polysaccharide-Based Nanocrystals: Chemistry and Applications:英文/黄进等主编. 一北京:化学工业出版社, 2015.3

(先进功能材料丛书)

ISBN 978-7-122-22984-7

[. ①聚··· II. ①黄··· III. ①聚多糖-纳米材料 IV. ①TB383

中国版本图书馆 CIP 数据核字(2015)第 022171 号

本书由化学工业出版社与德国 WILEY-VCH 出版公司合作出版。版权由化学工业出版社所有。本版本仅限在中华人民共和国境内(不包括中国台湾地区和中国香港、澳门特别行政区)销售。

字数 656 千字

责任编辑: 吴 刚 仇志刚

封面设计: 关 飞

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:北京京华虎彩印刷有限公司

710 mm×1000 mm 1/16 印张 20.5

2015 年 3 月北京第 1 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。

## "十二五"国家重点图书

## Advanced Functional Materials Series 先进功能材料从书

# Polysaccharide-Based Nanocrystals 聚多糖纳米晶



黄进 博士,现任武汉理工大学化学化工与生命科学学院教授,入选教育部新世纪优秀人才、江苏省高层次创新创业人才。研究领域涉及生物质资源高值化应用的材料化学基础,重点关注发展生物质基材料的化学与物理方法及关键技术,在利用纤维素、甲壳素、木质素、淀粉、植物蛋白等天然高分子研制生物基复合材料和先进材料方向开展了系列研究工作。已发表SCI收录论文100余篇(h-因子26),主编和参编中英文专著和教材7部,获国家发明专利授权40余项。



Peter R. Chang 博士,现任加拿大农业与农业食品(Agriculture and Agri-Food Canada)萨斯卡通研究中心研究员、萨斯喀彻温大学化学与生物工程系(Department of Chemical and Biological Engineering, University of Saskatchewan)教授。研究方向主要致力于发展支撑生物经济的生物质资源高效应用与产品研发的关键技术,重点关注农业生物质基聚合物的表征方法与加工技术,研制了多种生物基塑料、生物基复合材料与纳米复合材料、生物材料等及其它工业产品,参与指导了农业食品和生物资源工业领域众多国际公司的研发工作。发表SCI收录论文120余篇(h-因子29),完成了90余项工业技术转让,主编或参编专著多部,获发明专利授权4项。



林宁 博士,现任武汉理工大学化学化工与生命科学学院副教授。研究涉及生物质纳米粒子表面修饰方法学,重点关注聚多糖纳米晶复合材料体系的结构设计及其与性能的关系,致力于探索新材料在生物医学等领域的应用。发表SCI收录论文14篇,主编和参编中英文专著或教材4部。



Alain Dufresne 博士,现任法国格勒诺布尔国立综合理工学院(Grenoble Institute of Technology)造纸、印刷和生物材料国际学院(International School of Paper, Print Media and Biomaterials, Pagora)教授,曾任巴西里约热内卢联邦大学(Universidade Federal de Rio de Janeiro)和马来西亚国民大学(Universiti Kebangsaan Malaysia)客座教授。研究方向是利用来自可再生资源的纳米粒子研制高性能聚合物纳米复合材料,重点关注这类纳米复合材料的成型加工技术以及结构与性能表征与评价。发表学术论文200余篇(h-因子58),主编专著"Nanocellulose"并参编专著38部。

#### List of Contributors

#### Ishak Ahmad

School of Chemical Sciences and Food Technology Faculty of Science and Technology Universiti Kebangsan Malaysia (UKM) 43600, Bangi Selangor Malaysia

#### Debbie P. Anderson

BioProducts and Bioprocesses National Science Program Agriculture and Agri-Food Canada Government of Canada 107 Science Place Saskatoon SK S7N 0X2 Canada

#### Peter R. Chang

Bioproducts and Bioprocesses National Science Program Agriculture and Agri-Food Canada Government of Canada 107 Science Place Saskatoon SK S7N 0X2 Canada

#### and

Department of Chemical and Biological Engineering College of Engineering University of Saskatchewan Saskatoon SK S7N 5A9 Canada

#### Youli Chen

College of Chemistry, Chemical Engineering and Life Science Wuhan University of Technology Luoshi Road 122 Wuhan 430070 China

#### Alain Dufresne

The International School of Paper, Print Media, and Biomaterials (Pagora) Grenoble Institute of Technology (Grenoble INP) Domaine Universitaire, CS10065, 38402 Saint Martin d'Hères France

#### Shiyu Fu

State Key Laboratory of Pulp and Paper Engineering South China University of Technology Guangzhou 510641 China

#### Fei Hu

College of Chemistry, Chemical Engineering and Life Science Wuhan University of Technology Luoshi Road 122 Wuhan 430070 China

#### Jin Huang

College of Chemistry, Chemical Engineering and Life Science Wuhan University of Technology Luoshi Road 122 Wuhan 430070 China

#### Hanieh Kargarzadeh

School of Chemical Sciences and Food Technology Faculty of Science and Technology Universiti Kebangsaan Malaysia (UKM) 43600, Bangi Selangor Malaysia

#### Ning Lin

The International School of Paper, Print Media, and Biomaterials (Pagora) Grenoble Institute of Technology (Grenoble INP) Domaine Universitaire CS10065, 38402 Saint Martin d'Hères France

#### Hou-Yong Yu

College of Materials and Textile Zhejiang Sci-Tech University 928 Second Avenue, Xiasha Higher Education Zone Hangzhou 310018 China

#### Foreword

Since the beginning of the new century, the development of advanced biobased nanomaterials has been of significant interest in both academia and industry. Polysaccharide nanocrystals, mainly including rod-like cellulose nanocrystals, chitin nanowhiskers, and platelet-like starch nanocrystals, are highly crystalline rigid nanoparticles extracted from biosourced polymers that possess numerous advantages over inorganic nanoparticles. It has been reported that the diverse materials derived from polysaccharide nanocrystals will cover a broad range of properties that are useful in a wide range of applications, for example, in composites, electronics (flexible circuits), energy (flexible batteries, such as Li-ion and solar panels), packaging, coatings, detergents, adhesives, construction, pulp and paper, inks and printing, filtration, medicine and life science (scaffolds in tissue engineering, artificial skin and cartilage, wound healing, and vessel substitutes), optical devices (including reflective properties for security papers and UV or IR reflective barriers), rheological modifiers, and cosmetics. Since the first study on the use of cellulose nanocrystals as a reinforcing filler in nanocomposites about 20 years ago, a huge amount of literature has been devoted to research on polysaccharide nanocrystals in more than 1000 scientific publications.

As a relatively new research area, it is imperative to systematically assemble state-of-the-art technical accomplishments on polysaccharide nanocrystals, particularly with respect to physics, chemistry, materials science, processing, and engineering. This book covers extraction, structure, properties, and surface modification pertaining to polysaccharide nanocrystals. It provides an in-depth description of plastics and composites containing this unique biosourced nanoingredient in terms of structures, properties, manufacturing, and product performance. This book also describes the concept of functional nanomaterials based on polysaccharide nanocrystals and their potential applications. All chapters are contributed by leading experts who have both academic and professional credentials.

It is interesting to note that commercialization/utilization of polysaccharide nanocrystals (especially for cellulose nanocrystals) is finally catching on and is being pursued vigorously by industrial groups, notably in the United States, Canada, and Europe.

### XVI Foreword

Upcoming R&D and relentless pursuit represent well-justified challenges and opportunities for bringing the next generation of polysaccharide nanocrystal-based materials into reality.

#### **Preface**

Biobased Polysaccharide Nanocrystals: Chemistry and Applications is the first book that systematically describes the chemistry, properties, processing, and applications of polysaccharide nanocrystals and the nanocomposites/nanomaterials thereby derived.

Development of biobased materials has experienced fast growth in the past two decades thanks to public concern over the environment, climate change, and the depletion of fossil fuels. Over the last 10 years or so, this team of authors has worked collectively and separately with these interesting and yet little known renewable and biodegradable polysaccharide nanocrystals in the cutting edge field of functional nanomaterials and nanocomposites. As such, we are eager to share our knowledge and experience with readers and stakeholders, particularly researchers from academia and industry, policy makers, and the business sector, to foster rapid exploitation and commercialization of these fascinating bioingredients and their derived products, including but not limited to nanocomposites/nanomaterials.

This book is intended to give the reader a comprehensive overview of the present knowledge relating to extraction, structure, properties, surface modification, and the newly derived material of polysaccharide nanocrystals. In addition, it provides an in-depth description of plastics, composites, and nanomaterials specifically procured from cellulose nanocrystals, chitin nanowhiskers, and starch nanocrystals. This is an excellent book for scientists, engineers, graduate students, and industrial researchers in the field of polymeric materials. This book also covers the most recent progress with respect to: (i) the development of a conceptual framework of polysaccharide nanocrystals; (ii) numerous applications in the design and manufacture of nanocomposites and functional nanomaterials; and (iii) the relationship between structure and properties.

The authors sincerely thank Chemical Industry Press and Wiley-VCH press for their kind encouragement and support throughout the project and for publishing this book in both English and Chinese. In addition, the authors wish to acknowledge the continued support toward our research from the National

#### XVIII Preface

Natural Science Foundation of China (51373131, 31170549); Program of New Century Excellent Talents; Ministry of Education of China (NCET-11-0686); ecoENERGY Innovation Initiative of Canada; and the Program of Energy Research and Development (PERD) of Canada.

## Contents

List of Contributors XIIIForeword XVPreface XVII

1	Polysaccharide Nanocrystals: Current Status and Prospects in Material Science 1
	Jin Huang, Peter R. Chang, and Alain Dufresne
1.1	Introduction to Polysaccharide Nanocrystals 1
1.2	Current Application of Polysaccharide Nanocrystals in Material Science 3
1.3	Prospects for Polysaccharide Nanocrystal-Based Materials 8 List of Abbreviations 9 References 9
	References 9
2	Structure and Properties of Polysaccharide Nanocrystals 15 Fei Hu, Shiyu Fu, Jin Huang, Debbie P. Anderson, and Peter R. Chang
2.1	Introduction 15
2.2	Cellulose Nanocrystals 16
2.2.1	Preparation of Cellulose Nanocrystals 16
2.2.1.1	Acid Hydrolysis Extraction of Cellulose Nanocrystals 16
2.2.1.2	Effects of Acid Type 19
2.2.1.3	Effects of Pretreatment 24
2.2.2	Structure and Properties of Cellulose Nanocrystals 26
2.2.2.1	Structure and Rigidity of Cellulose Nanocrystals 26
2.2.2.2	Physical Properties of Cellulose Nanocrystals 32
2.3	Chitin Nanocrystals 41
2.3.1	Preparation of Chitin Nanocrystals 41
2.3.1.1	Extraction of Chitin Nanocrystals by Acid Hydrolysis 41
2.3.1.2	Extraction of Chitin Nanocrystals by TEMPO Oxidation 42
2.3.2	Structure and Properties of Chitin Nanocrystals 43
2.3.2.1	Structure and Rigidity of Chitin Nanocrystals 43
2.3.2.2	Properties of Chitin Nanocrystal Suspensions 45
2.4	Starch Nanocrystals 47

١	Contents	
	2.4.1	Preparation of Starch Nanocrystals 47
	2.4.1.1	Extraction of Starch Nanocrystals by Acid Hydrolysis 47
	2.4.1.2	Effect of Ultrasonic Treatment 49
	2.4.1.3	Effect of Pretreatment 50
	2.4.2	Structure and Properties of Starch Nanocrystals 50
	2.4.2.1	Structure of Starch Nanocrystals 50
	2.4.2.2	Properties of Starch Nanocrystal Suspensions 51
	2.5	Conclusion and Prospects 52
		List of Abbreviations 53
		References 54
	3	Surface Modification of Polysaccharide Nanocrystals 63
		Ning Lin and Alain Dufresne
	3.1	Introduction 63
	3.2	Surface Chemistry of Polysaccharide Nanocrystals 63
	3.2.1	Surface Hydroxyl Groups 63
	3.2.2	Surface Groups Originating from Various Extraction Methods 65
	3.3	Approaches and Strategies for Surface Modification 66
	3.3.1	Purpose and Challenge of Surface Modification 66
	3.3.2	Comparison of Different Approaches and Strategies of Surface
		Modification 67
	3.4	Adsorption of Surfactant 70
	3.4.1	Anionic Surfactant 70
	3.4.2	Cationic Surfactant 71
	3.4.3	Nonionic Surfactant 71
	3.5	Hydrophobic Groups Resulting from Chemical Derivatization 72
	3.5.1	Acetyl and Ester Groups with Acetylation and Esterification 72
	3.5.2	Carboxyl Groups Resulting from TEMPO-Mediated Oxidation 77
	3.5.3	Derivatization with Isocyanate Carboamination 79
	3.5.4	Silyl Groups Resulting from Silylation 79
	3.5.5	Cationic Groups Resulting from Cationization 81
	3.6	Polymeric Chains from Physical Absorption or Chemical
	261	Grafting 81
	3.6.1	Hydrophilic Polymer 82
	3.6.2	Polyester 83 Polyolefin 85
	3.6.3 3.6.4	Polyolefin 85 Block Copolymer 90
	3.6.5	Polyurethane and Waterborne Polyurethane 91
	3.6.6	Other Hydrophobic Polymer 92
	3.7	Advanced Functional Groups and Modification 92
	3.7.1	Fluorescent and Dye Molecules 94
	3.7.2	Amino Acid and DNA 95
	3.7.2	Self-Cross-linking of Polysaccharide Nanocrystals 95
	3.7.4	Photobactericidal Porphyrin Molecule 96
	3.7.5	Imidazolium Molecule 97
	3.7.10	ASSESSMENT OF WHAT AT A VAN V WAY Y

VIII

3.7.6 3.8	Cyclodextrin Molecule and Pluronic Polymer 97 Concluding Remarks 98
3.0	List of Abbreviations 98
	References 100
	References 100
4	Preparation of Polysaccharide Nanocrystal-Based
7	Nanocomposites 109
	Hou-Yong Yu, Jin Huang, Youli Chen, and Peter R. Chang
4.1	Introduction 109
4.2	Casting/Evaporation Processing 110
4.2.1	Solution Casting/Evaporation Processing 110
4.2.2	Solution Casting in Aqueous Medium 111
4.2.2.1	Dispersion Stability of Polysaccharide Nanocrystals in Aqueous
T. 2. 2. 1	Medium 111
4.2.2.2	Blending with Hydrophilic Polymers 112
4.2.2.3	Blending with Hydrophobic Polymers 116
4.2.3	Solution Casting in Organic Medium 117
4.2.3.1	Dispersion Stability of Polysaccharide Nanocrystals in Organic
4,2.5.1	Medium 117
4.2.3.2	Blending with Polymers in Organic Solvent 118
4.3	Thermoprocessing Methods 121
4.3.1	Thermoplastic Materials Modified with Polysaccharide
11012	Nanocrystals 121
4.3.2	Influence of Surface Modification of Polysaccharide Nanocrystals on
11012	Nanocomposite Thermoprocessing 122
4.4	Preparation of Nanofibers by Electrospinning Technology 127
4.4.1	Electrospinning Technology 127
4.4.1.1	Concepts 127
4.4.1.2	Formation Process of Nanofibers 128
4.4.1.3	Basic Electrospinning Parameters and Devices 129
4.4.1.4	Newly Emerging Electrospinning Techniques 130
4.4.2	Nanocomposite Nanofibers Filled with Polysaccharide
1.1.2	Nanocrystals 132
4.4.2.1	Electrospun Nanofibers in Aqueous Medium 132
4.4.2.2	Electrospun Nanofibers in Non-aqueous Medium 134
4.5	Sol-Gel Method 135
4.5.1	Concepts of Sol-Gel Process 135
4.5.2	Polysaccharide Nanocrystal-Based or -Derived Nanocomposites
1.5.2	Prepared by Sol-Gel Method 136
4.5.3	Chiral Nanocomposites Using Cellulose Nanocrystal Template 137
4.5.3.1	Inorganic Chiral Materials Based on Cellulose Nanocrystal
10.0.1	Template 137
4.5.3.2	Chiral Porous Materials 138
4.5.3.3	Chiral Porous Carbon Materials 141
4.5.3.4	Metal Nanoparticle-Decorated Chiral Nematic Materials 143

Contents	
4.6	Self-Assembly Method 144
4.6.1	Overview of Self-Assembly Method 144
4.6.2	Self-Assembly Method Toward Polysaccharide
	Nanocrystal-Modified Materials 145
4.6.2.1	Self-Assembly of Polysaccharide Nanocrystals in Aqueous
	Medium 145
4.6.2.2	Self-Assembly of Polysaccharide Nanocrystals in Organic
	Medium 148
4.6.2.3	Self-Assembly of Polysaccharide Nanocrystals in Solid Film 148
4.6.3	Polysaccharide Nanocrystal-Modified Materials Prepared by LBL
	Method 150
4.7	Other Methods and Prospects 152
310	List of Abbreviations 153
	References 154
	References 151
5	Polysaccharide Nanocrystal-Reinforced Nanocomposites 165
	Hanieh Kargarzadeh and Ishak Ahmad
5.1	Introduction 165
5.2	Rubber-Based Nanocomposites 166
5.3	Polyolefin-Based Nanocomposites 175
5.4	Polyurethane and Waterborne Polyurethane-Based
5.4	Nanocomposites 178
5.5	Polyester-Based Nanocomposites 192
5.6	Starch-Based Nanocomposites 200
5.7	Protein-Based Nanocomposites 204
5.8	Concluding Remarks 211
0.0	List of Abbreviations 211
	References 213
	Notice 210
6	Polysaccharide Nanocrystals-Based Materials for Advanced
	Applications 219
	Ning Lin, Jin Huang, and Alain Dufresne
6.1	Introduction 219
6.2	Surface Characteristics Induced Functional Nanomaterials 220
6.2.1	Active Groups 220
6.2.1.1	Importing Functional Groups or Molecules 220
6.2.1.2	Template for Synthesizing Inorganic Nanoparticles 222
6.2.2	Surface Charges and Hydrophilicity 225
6.2.2.1	Emulsion Nanostabilizer 225
6.2.2.2	High-Efficiency Adsorption 226
6.2.2.3	Permselective Membrane 226
6.2.3	Nanoscale and High Surface Area 227
6.2.3.1	Surface Cell Cultivation 227
6.2.3.2	Water Decontamination 227
6.3	Nano-Reinforcing Effects in Functional Nanomaterials 228

6.3.1	Soft Matter 229
6.3.1.1	Hydrogel 229
6.3.1.2	Sponge, Foam, Aerogel, and Tissue-Engineering Nanoscaffold 231
6.3.2	Special Mechanical Materials 233
6.3.3	Self-Healable and Shape-Memory Materials 236
6.3.4	Polymeric Electrolytes and Battery 237
6.3.5	Semi-conducting Material 238
6.4	Optical Materials Derived from Liquid Crystalline Property 239
6.5	Special Films and Systems Ascribed to Barrier Property 241
6.5.1	Drug Delivery – Barrier for Drug Molecules 242
6.5.2	Barrier Nanocomposites - Barrier for Water and Oxygen 244
6.6	Other Functional Applications 244
6.7	Concluding Remarks 244
	List of Abbreviations 245
	References 246
7	Characterization of Polysaccharide Nanocrystal-Based Materials 255
	Alain Dufresne and Ning Lin
7.1	Introduction 255
7.2	Mechanical Properties of Polysaccharide Nanocrystals 256
7.2.1	Intrinsic Mechanical Properties of Polysaccharide Nanocrystals 256
7.2.2	Mechanical Properties of Polysaccharide Nanocrystal Films 259
7.3	Dispersion of Polysaccharide Nanocrystals 261
7.3.1	Observation of Polysaccharide Nanocrystals in Matrix 263
7.3.2	Three-Dimensional Network of Polysaccharide Nanocrystals 266
7.4	Mechanical Properties of Polysaccharide Nanocrystal-Based
	Materials 269
7.4.1	Influence of the Morphology and Dimensions of the
	Nanocrystals 273
7.4.2	Influence of the Processing Method 274
7.5	Polysaccharide Nanocrystal/Matrix Interfacial Interactions 276
7.6	Thermal Properties of Polysaccharide Nanocrystal-Based
	Materials 281
7.6.1	Thermal Properties of Polysaccharide Nanocrystals 281
7.6.2	Glass Transition of Polysaccharide Nanocrystal-Based
	Nanocomposites 282
7.6.3	Melting/Crystallization Temperature of Polysaccharide
	Nanocrystal-Based Nanocomposites 283
7.6.4	Thermal Stability of Polysaccharide Nanocrystal-Based
	Nanocomposites 284
7.7	Barrier Properties of Polysaccharide Nanocrystal-Based
	Materials 284
7.7.1	Barrier Properties of Polysaccharide Nanocrystal Films 285

XII Contents	
7.7.2	Swelling and Sorption Properties of Polysaccharide
	Nanocrystal-Based Nanocomposites 286
7.7.3	Water Vapor Transfer and Permeability of Polysaccharide
	Nanocrystal-Based Nanocomposites 287
7.7.4	Gas Permeability of Polysaccharide Nanocrystal-Based
	Nanocomposites 288
7.8	Concluding Remarks 289
	List of Abbreviations 290
	References 291
	Application of the C

Index 301