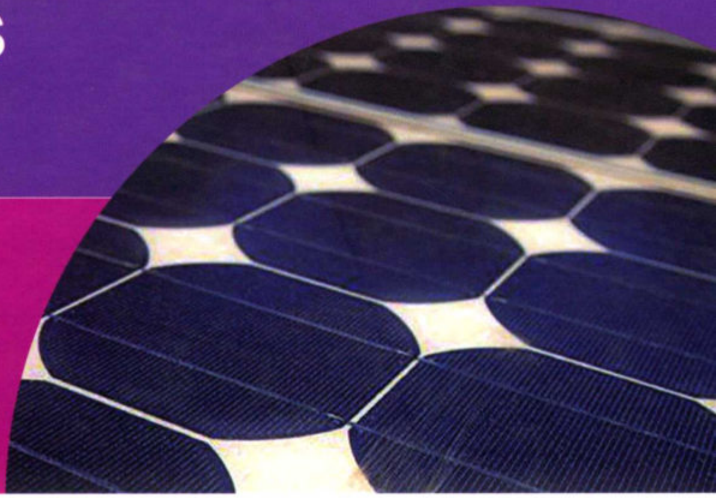
基于聚合物的多功能纳米复合材料（英文版）

Polymer-Based Multifunctional Nanocomposites and Their Applications



Kenan Song
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主编

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Authors:

Kenan Song
Advanced Materials Advanced Manufacturing Laboratory (AMAML),
Ira A. Fulton Schools of Engineering, Arizona State University, USA

Chuntai Liu
National Engineering Research Center for Advanced Polymer Processing
Technology, Zhengzhou University, China

John Zhanhu Guo
Integrated Composites Laboratory (ICL), Department of Chemical &
Biomolecular Engineering, University of Tennessee, USA

图书在版编目（CIP）数据

基于聚合物的多功能纳米复合材料：英文 / 宋克男（Kenan Song），刘春太（Chuntai Liu），（美）郭占虎（John Zhanhu Guo）主编. -- 北京：高等教育出版社，2019.9

ISBN 978-7-04-052588-5

Ⅰ.①基… Ⅱ.①宋… ②刘… ③郭… Ⅲ.①聚合物-纳米材料-复合材料-研究-英文 Ⅳ.①TB383

中国版本图书馆 CIP 数据核字（2019）第 187627 号

策划编辑 刘剑波　　责任编辑 刘占伟　　封面设计 杨立新
版式设计 徐艳妮　　责任印制 韩 刚

出版发行 高等教育出版社
社　　址 北京市西城区德外大街4号
邮政编码 100120
印　　刷 北京汇林印务有限公司
开　　本 787mm×1092mm 1/16
印　　张 21.75
字　　数 410 千字
购书热线 010-58581118
咨询电话 400-810-0598

网　　址 http://www.hep.edu.cn
　　　　 http://www.hep.com.cn
网上订购 http://www.hepmall.com.cn
　　　　 http://www.hepmall.com
　　　　 http://www.hepmall.cn

版　　次 2019 年 9 月第 1 版
印　　次 2019 年 9 月第 1 次印刷
定　　价 149.00 元

物 料 号 52588-00

Contributors

Numbers in parenthesis indicate the pages on which the authors' contributions begin.

Khalid A. Askar (111), Department of Materials Science and Engineering, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates

Adarsh Bafana (157), Nanobiomaterials and Bioprocessing Laboratory, Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX, United States

Tracy Benson (157), Operando Spectroscopy Laboratory, Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX, United States

David Bird (175), Interdisciplinary Program in Materials Science & Engineering, New Jersey Institute of Technology, Newark, NJ, United States

Linh Doan (157), Operando Spectroscopy Laboratory, Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX, United States

Xuehui Ge (1), The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, China

Natali Gendelberg (175), Interdisciplinary Program in Materials Science & Engineering, New Jersey Institute of Technology, Newark, NJ, United States

Haoqing Hou (201), Department of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, China

Clayton Jeffryes (157), Nanobiomaterials and Bioprocessing Laboratory, Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX, United States

Tuo Ji (77), Intelligent Composites Laboratory, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH, United States

Shaohua Jiang (201), College of Materials Science and Engineering, Nanjing Forestry University, Nanjing, China

Li Jin (201), Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, China

Weijun Li (261), State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, China

Yang Lu (157), Materials Engineering And Nanosensor [MEAN] Laboratory, Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL, United States

Nitin Mehra (77), Intelligent Composites Laboratory, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH, United States

Liwen Mu (77), Intelligent Composites Laboratory, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH, United States

Vladimir N. Popok (35), Department of Materials and Production, Aalborg University, Aalborg, Denmark

Nuggehalli M. Ravindra (175), Interdisciplinary Program in Materials Science & Engineering, New Jersey Institute of Technology, Newark, NJ, United States

Min Zhi Rong (137), Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, GD HPPC Lab, School of Chemistry, Sun Yat-Sen (Zhongshan) University, Guangzhou, China

Kenan Song (111), Department of Manufacturing Engineering, Arizona State University, Tempe, AZ, United States

Zhenhao Tian (1), The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, China

Yujun Wang (1), The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, China

Suying Wei (157), Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX, United States

Jia Wei (245), PCI Synthesis, Devens, MA, United States

Evan K. Wujcik (157), Materials Engineering And Nanosensor [MEAN] Laboratory, Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL, United States

Jianhong Xu (1), The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, China

Quan Xu (261), State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, China

Xing Yang (285), Viance LLC, Charlotte, NC, United states

Xiao Ji Ye (137), Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, GD HPPC Lab, School of Chemistry, Sun Yat-Sen (Zhongshan) University, Guangzhou; Guangdong Provincial Public Laboratory of Analysis and Testing Technology, China National Analytical Center, Guangzhou, China

Guoqiang Yu (157), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX, United States

Ming Qiu Zhang (137), Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, GD HPPC Lab, School of Chemistry, Sun Yat-Sen (Zhongshan) University, Guangzhou, China

Lin Zhang (201), Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, China

Wei Zhang (285), Sustainable Biomaterials Department, Virginia Tech, Blacksburg, VA, United States

Jiahua Zhu (77), Intelligent Composites Laboratory, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH, United States

Yong Zhu (137), Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, GD HPPC Lab, School of Chemistry, Sun Yat-Sen (Zhongshan) University, Guangzhou, China

Preface

Composite materials are those with multiple phases that display improved mechanical performance or functional properties. Polymer-based composites are based on polymer matrices and have applications in fields such as aerospace, automobiles, construction, biomedicine, catalysis, and electronics, among others. Despite all the potential these materials hold, a lack of development in novel fabrication methods, understanding of microstructural control, and bridging between theoretical predictions and experimental measurements remain significant hurdles to their widespread application.

In this book, we show novel approaches for preparing polymer nanocomposites (i.e., microfluidic technology in Chapter 1, cluster beam method in Chapter 2), property explorations (i.e., thermal conductivity in Chapter 3, multifunctional property in Chapter 4), microstructural creations (i.e., self-healing paths in Chapter 5), and novel applications (i.e., sensors for environmental monitoring in Chapter 6, biomedical applications in Chapter 7, electronics fields in Chapter 8, fuel cells in Chapter 9, adhesive systems in Chapter 10, and fire retardant materials in Chapter 11). This book aims to showcase recent advances in the field of polymer-based nanocomposites used for structural, thermal, electrical, optical, and other functional applications.

In Chapter 1, Xu's Group comprehensively reviews microfluidic technology in synthesizing nanoparticles and fabricating nanocomposites. The advantages of using this technology include the precise control of nanoparticle size and composition, temperature and mass transportation, and in situ screening and optimization of the manufacturing procedure. The authors cover the composition and structural management in nanoparticle and nanocomposite processing, as well as current applications and future perspectives.

In Chapter 2, Popok presents a state-of-the-art review of synthesizing metal and metal-oxide-included polymer composites. The author compares other widely used approaches with the cluster beam technique. Topics such as physical principles of cluster nucleation, growth and formation, polymer-nanoparticle interfacial interactions and immersions, and different methods in the use of cluster beams are provided. Following is a discussion of practical issues such as the application of polymer/metal and polymer/metal-oxide composites and future perspectives on the cluster beam technique.

In Chapter 3, Zhu's Group focuses on thermal conductivity between polymers and its composites. Study of the phonon is most fundamental to describe any heat conduction at the microscopic level. Nanoscale thermal conductivity depends on the development of efficient phonon transport pathways. Therefore, the improvement of thermal conductivity will correspond to phonons transportations without heat barriers or scattering. Understanding of thermal conductivity in polymer chains and across interface poses a challenge when carbon fillers, ceramic fillers, and metallic fillers are introduced in polymer matrices. Strategies to enhance thermal conduction are filler alignment, filler surface modifications, filler hybridizations, and so on.

Khalid's Group in Chapter 4 describes a multifunctional nanocomposite coating system that can be wear-resistant, optically transparent, self-cleaning, and self-healing. The coating materials obtained from simple spray-coating methods and their multiple functions rely on nanoparticle orientation modifications. Mechanical reinforcement and wear-resistance improvements are primarily correlated with the out-of-plane alignment of nanoparticles. Self-cleaning and self-healing functions are results of compatible thermoset-thermoplastic composites.

The Zhang Group discusses the self-pressurized healing system and mechanism in Chapter 5. The material system depends on the self-healing agent contained in micropipelines. In this way, the healing agent can flow without manual intervention. Epoxy/mercaptan healing agents and foaming agent filling in polypropylene tubes embeds in glass fiber/epoxy composites. Internal pressure is built up via the decomposition of the foaming agent and gas inflation. The pressurized healing fluid will burst out upon damage to tubes and initiate epoxy/hardener crosslinking. Healing efficiency designed in this way is significantly improved, and it may suggest many practical applications.

In Chapter 6, the Wujcik Group applied nanoscience and nanoengineering to sensors for environmental monitoring. The traditional environmental monitoring methods are UV-Vis, LC, GC, ICP-AES, F-AAS, and XRF. These analytical methods have a high cost, are time-consuming, and require pretraining; nanocomposite-based sensors, on the other hand, provide an alternative that is simple, cost-efficient, determined on-site, highly sensitive, and selective, and responds quickly. The group reviews monitoring of inorganic gases, carcinogenic gases, and organic gases in the air, soil monitoring, and organic pollutants and heavy metals in water. The chapter concludes with challenges and critical elements in developing nanocomposite sensors.

In Chapter 7, Ravindra's Group gives a brief overview of progress in nanocomposites in biomedical applications. Self-healing, biocompatibility, and mechanical durability, along with other properties, play critical roles in nanocomposites used in this field. Smart materials including biopolymers, shape memory polymers, and self-healing materials with different working mechanisms are comprehensively reviewed.

In Chapter 8, Jiang's Group concentrates on polymer-based nanocomposites with high dielectric permittivity. Polymer materials do not display dielectric properties, and dielectric/conductive fillers are introduced for high permittivity behaviors. This chapter presents the fundamentals of dielectrics, high permittivity in nanocomposites due to dielectric fillers, conductive fillers, and hybrid fillers, and fabrication methods of these composites. The chapter is concluded with outlooks, challenges, and future perspectives of nanocomposites with high dielectric permittivity.

Wei in Chapter 9 discusses the specific application of proton-conducting materials in polymer electrolyte members used in fuel cells. Starting from the fundamental proton transport mechanism in fuel cells and mechanisms of proton conducting, the author also reviews different types of fuel cells and fuel-cell-based electrolyte membranes. Current development of heterocycle-polymer systems for high-temperature polymer electrolyte membranes is introduced in detail.

Xu's Group in Chapter 10 reveals the advancement of smart adhesion surfaces, especially in gecko toe pad and mussel thread adhesion systems. The recent development of biomimicry adhesion systems, including polymers and other molecules, inspired by gecko toe pads and mussel threads, and their biomimicry applications are summarized.

Zhang in Chapter 11 reviews wood-polymer composites and their flame retardancy. The author starts from the fabrication techniques and characterization methods in making wood-polymer composites, followed by a review of phosphorus-based flame retardants, boron-based flame retardants, metal hydroxide flame retardants, graphite-based flame retardants, and multifiller-based flame retardants. The summary is concluded with challenges such as understanding the synergy effects of multiple flame retardants, burning behavior of wood-polymer composites, and requirement of regulatory fire tests.

This book is an attempt to collate information from a group of internationally known researchers and professors, and demonstrate the state-of-the-art of polymer-based nanocomposites regarding their design, fabrication, characterization, and applications. We would like to thank all the contributors for their willingness to participate in this exercise and being patient during the compilation work. The editor also wishes to thank the National Engineering Research Center for Advanced Polymer Processing Technology in Zhengzhou University, Integrated Composites Laboratory at University of Tennessee, and Advanced Materials Advanced Manufacturing Laboratory at Arizona State University for all the support.

Kenan Song
Chuntai Liu
John Zhanhu Guo

Contents

Chapter 1

Nanoparticles and Nanocomposites With Microfluidic Technology

Zhenhao Tian, Xuehui Ge, Yujun Wang and Jianhong Xu
The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, China

Chapter Outline

1.1 INTRODUCTION

Over the past few decades, chemically or physically synthesized nanoparticles and nanocomposites have drawn attention both in fundamental researches, and for practical applications. Compared to macro-size particles, nanoparticles and nanocomposites have unique physical and chemical properties, such as luminescent properties, photoelectric properties, catalytic properties, magnetic response, biocompatibility, and so on. Therefore, nanoparticles and nanocomposites have a wide range of applications in the fields of optical materials [1], semiconductor materials [1,2], catalysts [3,4], energy [5,6], bio-labels [7–10], drug deliveries [10], and many others. Therefore, it is

本书由高等教育出版社和 Elsevier 公司合作出版，并由 Elsevier 公司负责编辑加工和排版，故书中量和单位等难免存在不符合我国编辑出版规范之处。特此说明。

important to develop appropriate methods for the synthesis of nanoparticles and nanocomposites.

A wide variety of nanoparticles could be prepared by flask reactors or batch reactors [11–35]. In batch reactors, many methods and strategies have been developed to synthesize different kinds of nanoparticles and nanocomposites, such as reduction methods [13–16], sol-gel methods [17–20], hydrothermal methods [21–24], hot injection methods [25–30], multistep methods [31–35], and so on. For example, noble metal nanoparticles are synthesized via reduction methods. Au nanoparticles could be synthesized from $HAuCl_4$ reduced by sodium borohydride in the presence of surfactants [13]. Metal oxide nanoparticles are usually synthesized via sol-gel methods or hydrothermal methods. Fe_3O_4 could be obtained by sol-gel methods [19]. Under vigorous stirring, iron sources, $FeCl_3$ and $FeCl_2$, and a precipitator, aqueous ammonia, are added together to form Fe_3O_4 powders. In addition, the morphologies of ZnO nanoparticles can be controlled by changing the temperature and reaction time of hydrothermal reactions in batch reactors [23]. Quantum dots can be obtained via hot injection methods. Typically [25], Se precursors are injected into preheated Cd precursors, and then, the temperature is kept at around 260°C for nucleation and growth of CdSe quantum dots. Nanocomposites are often synthesized step by step according to different compositions and structures. For example, in order to synthesize ZnO/Ag core-shell nanoparticles [35], first, ZnO cores are synthesized through hydrothermal methods. Then, $AgNO_3$ is reduced to form silver layers. Therefore, the chemical system and research methods provided by the batch reactors provide a good example from which to learn.

No matter which methods or strategies for synthesis of nanoparticles in flask reactors are used, researchers often control the temperatures, residence times, precursor concentrations, ligands, feeding methods, and so forth to synthesize nanoparticles with different sizes or shapes. However, in conventional flask reactors, the temperature field and the concentration field are homogenized by means of rapid injection and stirring in a small volume [36]. Thus, the precise control of temperatures and concentrations is difficult, which can lead to the irreproducibility of sizes, size distributions, shapes, and quality of the nanomaterials from batch to batch [37]. In addition, for scaling up the yield of nanoparticles, simply expanding the volume of the reactor could make it difficult to maintain a homogeneous solvent environment [38]. So there are some drawbacks in the synthesis of nanoparticles via batch reactors.

As the mass and heat transfer efficiency in microfluidic devices are much higher than that in batch reactors [39–41], many methods based on microfluidic devices for nanoparticles and nanocomposites synthesis have been developed. In recent years, microfluidic devices have been widely used in chemical and biological fields. Due to efficient heat and mass transfers and spatial limitations in microfluidic devices, the size distribution of nanoparticles become more uniform [42]. Through convenient parameter adjustments in microreactors, nanoparticles with different sizes, shapes, and compositions could be synthesized reproducibility. In addition, because of the sealability in microreactors, many synthesis processes no longer needed inert gas protection, and solvent toxicity could be confined. In situ process monitoring, combined with transparent microchannels [43,44] could control the properties of nanoparticles and study the formation mechanism of nanoparticles conveniently.

In this review, we will firstly, introduce the types and fabrication techniques of microfluidic devices and the flow patterns commonly used for the preparation of nanoparticles. Then, the preparation methods and typical examples of organic nanoparticles, inorganic nanoparticles, and hybrid nanocomposites by using microreactors will be introduced, respectively.

1.2 MICROFLUIDIC PLATFORMS FOR NANOPARTICLES AND NANOCOMPOSITES SYNTHESIS

1.2.1 The Types and Fabrication Techniques of Microfluidic Platforms

The synthesis of nanoparticles by solvothermal methods, whether it is with a conventional flask reactor or microreactor, is necessary to control the reaction parameters, growth parameters, and crystallization parameters of the crystal system.

A uniform preparation environment, including uniformity of concentration and temperature, is critical for the synthesis of nanoparticles. In microreactors, the flow is laminar, and diffusion is the main pattern for mass and heat transfer. Due to the small size of the microreactors, the reactor volume is around a nanoliter or microliter, and the short diffusion distance and high specific surface area lead to efficient heat transfer and mass transfer. Thus, it is easy to obtain a uniform preparation environment in microreactors. The design of suitable microreactors and continuous preparation of controllable nanoparticles, depending on the preparation conditions of different nanoparticles, has been a popular topic in recent years.

Capillary reactors were first used to synthesize nanoparticles. Commonly used capillary microreactors were made of glass capillaries [45], PTFE tubes [46], stainless steel tubes [47,48], and so on. These materials are commercially available for easy fabricating and connection. In the glass capillary [45] (Fig. 1.1A), researchers achieved the preparation of the emulsion [52–54]. In addition, because the glass capillary is transparent, online characterization and online light curing facilitated the preparation of nanoparticles. Temperature and pressure for the glass capillary micro-reaction have some restrictions; generally the reaction processes take place under normal temperature and pressure. Polytetrafluoroethylene tubes [46] with excellent chemical stability, that are soft and easy to bend, and have a certain heat resistance, are commonly used