炭材料科学与工程
——从基础到应用

Carbon Materials Science and Engineering
——From Fundamentals to Applications

Michio Inagaki（日本 稻垣道夫）
Kang Feiyu（中国 康飞宇）
著

Tsinghua University Press 清华大学出版社

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藏书章

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内容简介

近年来由于富勒烯和碳纳米管的发现，炭材料研究受到了全球材料科学界、物理界和化学界的广泛关注。该书系统地介绍了炭材料的科学理论知识和工程应用实例。第一部分为绪论，介绍了写作本书的目的和炭材料的分类与发展史，以及炭的多样性。第二部分为炭材料的基础科学知识，主要介绍了炭材料的结构、性能和制备工艺，特别是炭化和石墨化的原理及其微观结构控制技术，多孔炭的孔径控制和炭材料掺杂其他原子的技术，炭材料的各类表征方法。第三部分主要为炭素材料的工程与应用问题，特别是新型炭材料的发展及其在能源、环保、原子能、国防方面的应用实例，涉及石墨电极，高密度各向同性石墨，高取向热解石墨，玻璃炭，纤维状炭，多孔炭，石墨层间化合物等。

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Abstract

Carbon materials have attracted much attention, especially fullerenes and carbon nanotubes. However, carbon materials have been used since prehistoric era with a wide variety of structures and functions. This book describes fundamentals of carbon materials in Part 2, after an introduction to the history of carbon materials in Part 1. Part 3 discusses engineering problems of carbon materials with focus on their preparation, function and applications.

Part 1 introduces and explains the carbon families of diamond, graphite, fullerenes and carbyne on the basis of their carbon-carbon bonds.

Part 2 analyzes the characteristics of the carbon families in terms of their structure and properties by dividing the formation process into a texture formation stage (carbonization) and a structural development stage (graphitization). Novel techniques are given to relate the carbonization and graphitization stages. In addition, pore development and the introduction of foreign species into the various carbon materials were reviewed. Part 2 includes 8 chapters, carbon families, structure and texture, texture development (carbonization), novel techniques for carbonization, structure development (graphitization), acceleration of graphitization, pore development, and introduction of foreign species into carbon materials.

Part 3 describes engineering applications of carbon materials, most of which have been widely used in industries and houses. Some of these applications have contributed greatly to the development of modern technology and will be used widely in the future. Part 3 includes 9 chapters, graphite electrodes and high-density isotropic graphite, highly-oriented graphite, amorphous glass-like carbons,

fibrous carbons including carbon fibers, carbon nanotubes and nanofibers, porous carbons including activated carbons, carbon-based composites, intercalation compounds, carbon materials for energy storage including lithium ion rechargeable batteries, electrochemical capacitors, hydrogen and methane storage, and carbon materials for environment remediation including carbon/anatase composites, exfoliated graphite for heavy oil sorption.

This book seeks to give readers a general understanding of the wide variety of carbon materials from graphite to carbon nanotubes. Therefore, the most interested readers will be those who just started or are going to start work on carbon materials.

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Preface

In 1985, one of the authors (M. Inagaki) published a book entitled *Materials Engineering of Carbons* in Japanese (Nikkan Kogyo Shinbun-sya, 238 pages). It was just before the discovery of buckminsterfullerenes C_{60}, in other words, the attention of the people was not yet directed to nanocarbons at that time. In the book, he already emphasized the importance of nanotexture in carbon materials belonged to the graphite family and discussed carbonization and graphitization of carbon materials on the basis of their nanotextures, planar, axial, point and random orientation schema. The discovery of various fullerenes and later carbon nanotubes opened a new era for carbon materials, not only graphitic carbon materials with planar structure and three dimensional diamond structure, but also nano-sized clusters, fullerenes, with closed structures containing pentagons of carbon atoms and tubular carbons with nano-sized diameters consisting of a single curved hexagon layer of carbon atoms are possible. The discovery of single-wall and multi-walled carbon nanotubes stimulated the interest of scientists and engineers in the fields related to nanotechnology. At almost the same period, various new applications of carbon materials in the graphite family were also developed: anode materials for lithium ion rechargeable batteries, carbon fibers for remediation of water environment, electric double layer capacitors for energy storage using activated carbon electrodes, etc. In 1994, therefore, he published another book in Japanese entitled *New Carbon Materials-Structure and Functions* (Gihoudo Shuppan, 202 pages) with his friend Prof. Yoshihiro Hishiyama of Musashi Institute of Technology. In their book, properties and applications of different carbon materials, including

fullerenes and carbon nanotubes, were described. However, progress in science, engineering and applications of carbon materials was so rapid all over the world that he decided to publish the book in English: *New Carbons -Control of Strcuture and Functions* (2000, Elsevier, 229 pages). In the book, he focused mostly on the engineering of new carbon materials based on hexagonal networks of carbon atoms.

Recently, the authors strongly felt that, even though many young scientists and engineers were interesting in and working on nanocarbons, such as carbon nanotubes, basic knowledge on carbon materials is necessary for them. Most of the basics of carbon materials were already clarified before 1985. The books, which give such fundamental knowledge on carbon materials are rather few and also they must be handy and easy to buy. This is why the authors decided to publish the present book at Tsinghua University Press, which is aiming to give comprehensive information firstly on fundamental science about preparation and characterization of various carbon materials, and secondary on engineering and applications of various carbon materials. Basic concept of the present book is the same as those published by one of authors (M. Inagaki), *i. e.*, classifications based on carbon families and nanotextures.

The authors hope to provide fundamental science and engineering on carbon materials and some applications, even though the newest ones cannot be included because of so fast development in this field, to young people, graduate students who are working on various carbon materials and engineers whose works are more or less related to carbon materials. It will be a great pleasure for the authors if they will bring this book with them to discuss their results and to read the scientific papers published. They may find out how the data they got and/or those published do either agree or disagree with the general information explained in this book, and also what are missing in this book.

Michio Inagaki
(Aichi Institute of Technology, Japan)
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(Tsinghua University, P. R. China)
2006.4

前　言

本文作者之一稻垣道夫教授于1985年在日本出版了一本《炭的材料工程》，那是在富勒烯 C_{60} 发现之前，更是在碳纳米管发现之前了。但是作者在书中已经强调了炭材料纳米结构的重要性，而且讨论了基于纳米取向排列的炭化和石墨化原理，即具有不同面取向、轴取向、点取向和无序排列的碳/石墨构成了石墨材料大家族。随后，各种富勒烯和碳纳米管的发现，开辟了炭材料研究的新方向，不但可以控制有面取向结构的石墨、有三维排列的金刚石，而且在纳米尺度上合成含有碳原子五环结构的富勒烯和含有单层弯曲密排六方碳原子的碳纳米管。单壁和多壁碳纳米管的发现将科学家和工程师们的注意力引入了一个崭新的研究领域——纳米技术。与此同时，石墨家族中各类炭材料的新应用也得到了开发，如锂离子二次电池阳极材料，炭纤维对水环境的修复和保护，以活性炭电极为主的储能器件——超级电容器，等等。因此，稻垣教授在1994年又和他的朋友武藏工业大学菱山幸宥教授合作出版了日文版的《新型炭材料——结构与功能》。在该书中，他们对包括富勒烯和碳纳米管在内的各种炭材料的功能和应用进行了介绍。然而，科学技术日新月异，炭材料的工程与应用在全世界得到了快速发展，稻垣教授于2000年又出版了英文版的《新型炭材料——结构和功能的控制》(*New Carbons—Control of Strcuture and Functions* (2000, Elsevier))。该书着重介绍了基于碳原子密排六方网络结构的新型炭材料的工程应用。

近年来，稻垣教授受聘为清华大学的客座教授，他和本书的另一作者——康飞宇教授共同为清华大学的研究生和本科生开设了“新型炭材料”课程。作者深深感受到许多年轻科研工作者对纳米炭材料十分感兴趣，比如碳纳米管，但是对大多数人来说，了解炭材料的基础知识也是十分迫切和重要的。稻垣教授以前出版的著作中关于该方面的基础知识介绍相对较少，而且对年轻人来说，购买那些国外出版的书确实贵了些。因此，作者决定在清华大学出版社与康飞宇教授共同出版一本书，该书首先介绍各类炭材料在制备和表征方面的综合性基础知识，其次是它们的工程与应用示例。比如炭材料家族的分类

和碳纳米结构方面。

炭材料由于其结构的多样性，导致其性能的多样化，在环保、能源、制造业、国防等领域得到了广泛的应用。该书主要目的是向读者系统介绍炭材料的科学理论知识和工程应用实例。本书共分为三部分：第一部分为绪论，介绍了写作本书的目的和炭材料的分类与发展史，炭材料的多样化；第二部分为炭材料的基础科学问题，主要介绍炭材料的结构，性能和制备工艺，特别是炭化和石墨化的原理以及它的微观结构控制技术，多孔炭和孔径控制新技术和其他原子与炭材料相结合的技术；第三部分主要为炭材料的工程与应用问题，特别是新型炭材料的发展及其在储能、环保、原子能、军工方面的应用实例，涉及的炭材料有石墨电极、高密度各向同性石墨、高取向热解石墨、玻璃炭、纤维状炭、多孔炭、石墨层间化合物，等等。

作者虽然希望能够为年轻炭材料科研工作者提供有关炭材料及其应用的科学与工程的基础知识，但是并不能在一本书中包含所有炭材料的最新研究成果。如果青年人能够经常阅读本书并且能够和他们自己的最新成果开展对比和讨论，他们也许会发现本书中的一些数据和结果与他们自己的结果不符合，甚至不准确，或者解释不全面，但是如果能够起到这样的作用，作者也就会感到由衷的高兴。

日本爱知工业大学教授　稻垣道夫

中国北京清华大学教授　康飞宇

2006 年 4 月

Contents

1 Introduction 1

1.1 Carbon Materials 3

1.2 Short History of Carbon Materials 7

References 8

1.3 Classic Carbons, New Carbons and Nanocarbons 9

1.3.1 Classic carbons 9

1.3.2 New carbons 10

1.3.3 Nanocarbons 14

References 16

1.4 Construction and Purposes of the Present Book 18

2 Fundamentals of Carbon Materials 21

2.1 Carbon Families 23

2.1.1 Carbon-carbon bonds 23

2.1.2 Carbon families 25

2.1.3 Relations to neighboring atoms 29

2.2 Structure and Texture of Carbon Materials 32

2.2.1 Structure 32

2.2.2 Structural development with heat treatment (Carbonization and graphitization) 37

2.2.3 Nanotexture 40

2.2.4 Microtexture (Agglomeration) 44

References 45

2.3 Nanotexture Development in Carbon Materials (Carbonization) 47
2.3.1 Formation processes of carbon materials 47
2.3.2 Gas phase carbonization 49
2.3.3 Solid phase carbonization 63
2.3.4 Liquid phase carbonization 75
References 86
2.4 Novel Techniques for Carbonization 90
2.4.1 Template method 90
2.4.2 Polymer blend method 94
2.4.3 Pressure carbonization 96
2.4.4 High yield carbonization 102
2.4.5 Low temperature carbonization 106
References 109
2.5 Structural Development in Carbon Materials (Graphitization) 112
2.5.1 Structure parameters 112
2.5.2 Graphitization behavior 120
2.5.3 Carbon materials with planar orientation 122
2.5.4 Carbon materials with axial orientation 134
2.5.5 Carbon materials with point orientation 139
2.5.6 Carbon materials with random orientation 143
2.5.7 Relations among structure parameters 146
2.5.8 Graphitization process 151
2.5.9 Graphitizing and non-graphitizing carbons 157
2.5.10 Heterogeneous graphitization (Multiphase graphitization) 160
References 164
2.6 Acceleration of Graphitization 167
2.6.1 Catalytic graphitization 167
2.6.2 Stress graphitization 171
2.6.3 Graphitization of exfoliated carbon fibers 179
References 182
2.7 Pore Development in Carbon Materials 184
2.7.1 Pores in carbon materials 184

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2.7.2 Identification of pores in carbon materials 187
2.7.3 Pore development in carbon materials 202
References 223
2.8 Introduction of Foreign Species 226
2.8.1 Possibility to introduce foreign species into carbon materials 226
2.8.2 Intercalation 227
2.8.3 Substitution 246
2.8.4 Doping 254
2.8.5 Dispersion of fine metal particles 258
References 262

3 Engineering and Applications of Carbon Materials 267

3.1 Polycrystalline Graphite Blocks 269
3.1.1 Production 269
3.1.2 Applications 275
3.1.3 Filler cokes and binder pitches 283
3.1.4 Properties 293
References 305
3.2 Highly-oriented Graphite 307
3.2.1 Highly-oriented graphite 307
3.2.2 Kish graphite 308
3.2.3 Highly-oriented pyrolytic graphite (HOPG) 312
3.2.4 Graphite films derived from polyimide films 316
3.2.5 Flexible graphite sheets 331
References 341
3.3 Non-graphitizing and Glass-like Carbons 343
3.3.1 Structural characteristics 343
3.3.2 Properties 349
3.3.3 Glass-like carbons 354
References 357

3.4 Fibrous Carbons 359
3.4.1 Classification of fibrous carbons 359
3.4.2 Carbon fibers 360
3.4.3 Carbon nanotubes and nanofibers 391
3.4.4 Single wall carbon nanohorns 406
3.4.5 Carbon microcoils 408
References 410
3.5 Porous Carbons 414
3.5.1 Activated carbons 414
3.5.2 Novel techniques to control pore structure 421
3.5.3 Exfoliated graphite 439
References 444
3.6 Carbon-based Composites 449
3.6.1 Carbon-based composites 449
3.6.2 Carbon/carbon composites (C/Cs) 450
3.6.3 Carbon fiber reinforced plastics 462
3.6.4 Carbon/ceramics composites 466
3.6.5 Carbon/metal composites 482
References 483
3.7 Intercalation Compounds 485
3.7.1 Possible applications 485
3.7.2 High conductivity function 487
3.7.3 Electrochemical functions 492
3.7.4 Catalytic functions 500
3.7.5 Gas adsorption and storage 502
3.7.6 Other functions 508
References 511
3.8 Carbon Materials for Energy Storage 514
3.8.1 Rechargeable batteries 514
3.8.2 Electrochemical capacitors 524
3.8.3 Storage of hydrogen gas 538
3.8.4 Storage of methane gas 545

3.8.5 Applications to other batteries 549

References 550

3.9 Carbon Materials for Environment Remediation 554

3.9.1 Carbon/anatase composites 554

3.9.2 Carbon materials for sorption of viscous fluids 572

3.9.3 Carbon fibers 595

References 599

Acknowledgements 603

Subject Indexes 604

1 Introduction

1.1 Carbon Materials

Carbon C is one of the abundant elements on the earth. Almost all organics are composed of carbon networks, and carbon materials are very familiar in our daily lives, for example, ink for newspapers, "lead" for pencils, activated carbon in refrigerators, *etc.* Carbon materials, which consist mainly of carbon atoms, have been used since the prehistoric era as charcoal. In Japan, a large amount of charcoal (about 800 tons) was reported to be used for casting a great image of Buddha in Nara from 747 to 750. Soft graphite has been used for a long time as "lead" and carbon blacks as black inks. Diamond crystals, fascinating for all human beings not only as jewels but also the hardest material, were found to consist of carbon atoms, the same atoms as lubricating soft graphite, not so long ago, in 1799. Nowadays various carbon materials are used in our daily lives, though many of them are inconspicuous, activated carbon produced from coconut shells as a filter of tobacco, carbon fibers for reinforcement of rackets and fishing rods, "lead" for automatic pencils, activated carbon for deodorizing refrigerators, membrane switches for computer keyboards and various equipments, *etc.*

Charcoal may be the first carbon materials used practically, since the prehistoric age. Carbon materials began to be used as electrodes for batteries around 1800 and around 1878 large-sized carbon rods were used as electrodes for iron refining. These electrodes were industrially produced by heat-treatment at high temperatures, as high as 3000 ℃, and called graphite electrodes because crystalline graphite structure was well developed in most of them. In charcoal mentioned above, however, no graphite structure was developed and it was said to have amorphous structure. Later on, various carbon materials having graphite structure which have been called graphite materials, and their applications were developed, even though graphite structure developed only in small proportions. At the same time, carbon materials without noticeable graphite structure were also developed and opened new applications.

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