

传感材料与传感技术丛书

Sensing Material and Sensing Technology Series

# 化学传感器：传感材料基础

第4册

## 多孔纳米材料的特性及应用

CHEMICAL SENSORS:  
FUNDAMENTALS OF SENSING MATERIALS

The Characteristics and Applications of Porous Nanomaterials

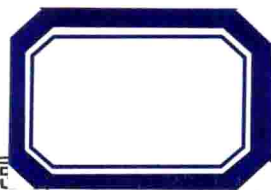
Ghenadii Korotcenkov 主编

影印版



哈尔滨工业大学出版社  
HARBIN INSTITUTE OF TECHNOLOGY PRESS

传感材料与传感



# 化学传感器：传感材料基础

第4册

## 多孔纳米材料的特性及应用

影印版

Ghenadii Korotcenkov 主编



哈尔滨工业大学出版社  
HARBIN INSTITUTE OF TECHNOLOGY PRESS

# 黑版贸审字08-2013-062号

Ghenadii Korotcenkov

Chemical Sensors: Fundamentals of Sensing Materials, Vol 2: Nanostructured Materials

9781606501061

Copyright © 2010 by Momentum Press, LLC

All rights reserved.

Originally published by Momentum Press, LLC

English reprint rights arranged with Momentum Press, LLC through McGraw-Hill Education (Asia)

**This edition is authorized for sale in the People's Republic of China only, excluding Hong Kong, Macao SAR and Taiwan.**

本书封面贴有McGraw-Hill Education公司防伪标签,无标签者不得销售。

版权所有,侵权必究。

## 图书在版编目(CIP)数据

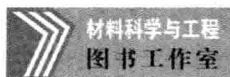
多孔纳米材料的特性及应用 = The Characteristics and Applications of Porous Nanomaterials : 英文 / (摩尔)科瑞特森科韦 (Korotcenkov, G.) 主编. — 影印本. — 哈尔滨: 哈尔滨工业大学出版社, 2013.9

(传感材料与传感技术丛书; 化学传感器: 传感材料基础 4)

ISBN 978-7-5603-4152-1

I. ①多… II. ①科… III. ①多孔性材料-纳米材料-研究-英文 IV. ①TB383

中国版本图书馆CIP数据核字(2013)第147632号



责任编辑 杨桦 许雅莹 张秀华

出版发行 哈尔滨工业大学出版社

社址 哈尔滨市南岗区复华四道街10号 邮编 150006

传真 0451-86414749

网址 <http://hitpress.hit.edu.cn>

印刷 哈尔滨市工大节能印刷厂

开本 787mm × 960mm 1/16 印张 12.5

版次 2013年9月第1版 2013年9月第1次印刷

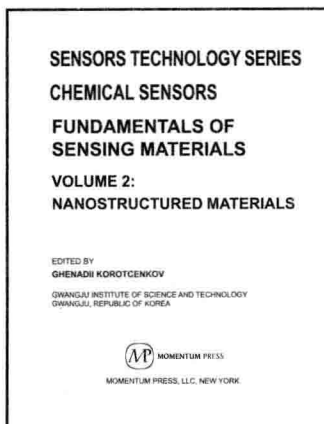
书号 ISBN 978-7-5603-4152-1

定价 58.00元

(如因印刷质量问题影响阅读,我社负责调换)

## 影印版说明

1. 《传感材料与传感技术丛书》为MOMENTUM PRESS的*SENSORS TECHNOLOGY SERIES*的影印版。考虑到使用方便以及内容统一，将原系列6卷分为10册影印。本册是



5~8章的内容。

2. 原版各卷的文前介绍、索引、封底内容在其对应的影印版分册中均完整呈现。

3. 各册均给出中文参考目录，方便读者快速浏览。

4. 各册在页脚重新编排页码，该页码对应中文参考目录。保留了原版页眉及页码，其页码对应原书目录及索引。

5. 各册的最后均给出《传感材料与传感技术丛书》的书目及各册的章节目录。

材料科学与工程图书工作室

联系电话 0451-86412421

0451-86414559

邮箱 yh\_bj@aliyun.com

xuyaying81823@gmail.com

zhxh6414559@aliyun.com

# **PREFACE TO CHEMICAL SENSORS: FUNDAMENTALS OF SENSING MATERIALS**

Sensing materials play a key role in the successful implementation of chemical and biological sensors. The multidimensional nature of the interactions between function and composition, preparation method, and end-use conditions of sensing materials often makes their rational design for real-world applications very challenging.

The world of sensing materials is very broad. Practically all well-known materials could be used for the elaboration of chemical sensors. Therefore, in this series we have tried to include the widest possible number of materials for these purposes and to evaluate their real advantages and shortcomings. Our main idea was to create a really useful “encyclopedia” or handbook of chemical sensing materials, which could combine in compact editions the basic principles of chemical sensing, the main properties of sensing materials, the particulars of their synthesis and deposition, and their present or potential applications in chemical sensors. Thus, most of the materials used in chemical sensors are considered in the various chapters of these volumes.

It is necessary to note that, notwithstanding the wide interest and use of chemical sensors, at the time the idea to develop these volumes was conceived, there was no recent comprehensive review or any general summing up of the fundamentals of sensing materials. The majority of books published in the field of chemical sensors were dedicated mainly to analysis of particular types of devices. This three-volume review series is therefore timely.

This series, *Chemical Sensors: Fundamentals of Sensing Materials*, offers the most recent advances in all key aspects of development and applications of various materials for design of chemical sensors. Regarding the division of this series into three parts, our choice was to devote the first volume to the fundamentals of chemical sensing materials and processes and to devote the second and third volumes to properties and applications of individual types of sensing materials. This explains why, in *Volume 1: General Approaches*, we provide a brief description of chemical sensors, and then detailed discussion of desired properties for sensing materials, followed by chapters devoted to methods of synthesis, deposition, and modification of sensing materials. The first volume also provides general background information about processes that participate in chemical sensing. Thus the aim of this volume, although not exhaustive, is to provide basic knowledge about sensing materials, technologies used for their preparation, and then a general overview of their application in the development of chemical sensors.

Considering the importance of nanostructured materials for further development of chemical sensors, we have selected and collected information about those materials in *Volume 2: Nanostructured Materials*. In this volume, materials such as one-dimension metal oxide nanostructures, carbon nanotubes, fullerenes, metal nanoparticles, and nanoclusters are considered. Nanocomposites, porous semiconductors, ordered mesoporous materials, and zeolites also are among materials of this type.

*Volume 3: Polymers and Other Materials*, is a compilation of review chapters detailing applications of chemical sensor materials such as polymers, calixarenes, biological and biomimetic systems, novel semiconductor materials, and ionic conductors. Chemical sensors based on these materials comprise a large part of the chemical sensors market.

Of course, not all materials are covered equally. In many cases, the level of detailed elaboration was determined by their significance and interest shown in that class of materials for chemical sensor design.

While the title of this series suggests that the work is aimed mainly at materials scientists, this is not so. Many of those who should find this book useful will be “chemists,” “physicists,” or “engineers” who are dealing with chemical sensors, analytical chemistry, metal oxides, polymers, and other materials and devices. In fact, some readers may have only a superficial background in chemistry and physics. These volumes are addressed to the rapidly growing number of active practitioners and those who are interested in starting research in the field of materials for chemical sensors and biosensors, directors of industrial and government research centers, laboratory supervisors and managers, students and lecturers.

We believe that this series will be of interest to readers because of its several innovative aspects. First, it provides a detailed description and analysis of strategies for setting up successful processes for screening sensing materials for chemical sensors. Second, it summarizes the advances and the remaining challenges, and then goes on to suggest opportunities for research on chemical sensors based on polymeric, inorganic, and biological sensing materials. Third, it provides insight into how to improve the efficiency of chemical sensing through optimization of sensing material parameters, including composition, structure, electrophysical, chemical, electronic, and catalytic properties.

We express our gratitude to the contributing authors for their efforts in preparing their chapters. We also express our gratitude to Momentum Press for giving us the opportunity to publish this series. We especially thank Joel Stein at Momentum Press for his patience during the development of this project and for encouraging us during the various stages of preparation.

Ghenadii Korotcenkov

# **PREFACE TO**

## ***VOLUME 2: NANOSTRUCTURED MATERIALS***

Nanomaterials and nanotechnology are new fields of science and technology. Fundamentally, nanotechnology is about manipulating and making materials at the atomic and molecular levels. It is expected that nanotechnology will change solid-state gas sensing dramatically and will probably gain importance in all fields of sensor application over the next 10 to 20 years. Nanotechnology is still in its infancy, but the field has been a hot area of research globally since a few years ago. It has been found that with reduction in size, novel electrical, mechanical, chemical, catalytic, and optical properties can be introduced. As a result, it has been concluded that one-dimensional structures will be of benefit for developing new-generation chemical sensors that can achieve high performance. Therefore, in the last decade, the study of 1-D materials has become a primary focus in the field of chemical sensor design. Synthesis of new nano objects and exploitation of their extraordinary properties is the goal and dream of many researchers engaged in the field of sensor design. In addition, it has also been established that 1-D structures may be ideal systems in which to study the nature of chemical sensing effects.

Although many people consider this a brand-new technology yielding cutting-edge applications for consumer products, researchers have in fact been working in the field of catalysis and gas-sensing effects for decades. What we call nanoparticle technology today actually began in the era of the 1950s–1980s, and chemical catalysis and gas sensor research and development have been conducted at the nanoscale ever since. Initially, research labs used the technology to increase the efficiency of heterogeneous catalysis and to improve the sensitivity of solid-state gas sensors. Nanoclusters of metal catalysts and nanograins of metal oxides with dimensions less than 10 nm were the main objects of research.

The recent development of advanced tools for characterizing materials at the nano- or subnanoscale has provided scientists with new insights for understanding and improving existing devices and clues for ways to design new nanostructured materials to make better catalysts and sensors. Recent research has thus led to new types of prospective nanostructured materials.

It is obviously difficult to cover all aspects of a dynamic research area such as nanotechnology. Of course, it is not possible to analyze in one volume every nanoparticulate matter and its role in the revolution of materials for chemical sensor applications. However, we have tried to cover this field more or less completely. This book, together with Volume 1, includes as much as possible the recent advances and breakthroughs in the area of nanomaterials for chemical sensors as achieved by research groups all over the world. These contributions have led to the emergence of some general guidelines.

This book includes eight chapters written by researchers who are at the forefront of their field, which address the role of nanomaterials in chemical sensors. One-dimensional metal oxide structures, carbon nanotubes, fullerenes, and metal nanoparticles are the objects of detailed analysis in the present volume. Processing, properties, and applications of porous semiconductors, zeolites, nanocomposites and ordered mesoporous materials are also discussed in this volume. A brief history of nanotechnology, particulars of nanomaterial properties, specificity, and future trends in nanotechnology can be found in this volume as well.

Ghenadii Korotcenkov



## ABOUT THE EDITOR

***Ghenadii Korotcenkov*** received his Ph.D. in Physics and Technology of Semiconductor Materials and Devices in 1976, and his Habilitate Degree (Dr.Sci.) in Physics and Mathematics of Semiconductors and Dielectrics in 1990. For a long time he was a leader of the scientific Gas Sensor Group and manager of various national and international scientific and engineering projects carried out in the Laboratory of Micro- and Optoelectronics, Technical University of Moldova. Currently, he is a research professor at Gwangju Institute of Science and Technology, Gwangju, Republic of Korea.

Specialists from the former Soviet Union know G. Korotcenkov's research results in the study of Schottky barriers, MOS structures, native oxides, and photoreceivers based on Group III–V compounds very well. His current research interests include materials science and surface science, focused on metal oxides and solid-state gas sensor design. He is the author of five books and special publications, nine invited review papers, several book chapters, and more than 180 peer-reviewed articles. He holds 16 patents. He has presented more than 200 reports at national and international conferences. His articles are cited more than 150 times per year. His research activities have been honored by the Award of the Supreme Council of Science and Advanced Technology of the Republic of Moldova (2004), The Prize of the Presidents of Academies of Sciences of Ukraine, Belarus and Moldova (2003), the Senior Research Excellence Award of Technical University of Moldova (2001, 2003, 2005), a Fellowship from the International Research Exchange Board (1998), and the National Youth Prize of the Republic of Moldova (1980), among others.

# CONTRIBUTORS

**Tarushee Ahuja** (Chapter 8)

Department of Applied Chemistry  
Delhi College of Engineering  
University of Delhi  
Bawana Road  
Delhi-110042, India

**Pai-Chun Chang** (Chapter 2)

Department of Physics  
and Department of Electrical Engineering  
University of Southern California  
Los Angeles, California 90089-0484, USA

**Beongki Cho** (Chapter 1)

Department of Material Science and Engineering  
and Department of Nanobio Materials and Electronics  
Gwangju Institute of Science and Technology  
Gwangju, 500-712, Republic of Korea

**Hossam Haick** (Chapter 4)

Department of Chemical Engineering  
and Russell Berrie Nanotechnology Institute  
Technion—Israel Institute of Technology  
Haifa 32000, Israel

**Ghenadii Korotcenkov** (Chapters 1 and 5)

Department of Material Science and Engineering  
Gwangju Institute of Science and Technology  
Gwangju, 500-712, Republic of Korea

*and*

Technical University of Moldova  
Chisinau, 2004, Moldova

**Gregg P. Kotchey** (Chapter 3)

Department of Chemistry  
University of Pittsburgh and the National Energy Technology Laboratory  
Pittsburgh, Pennsylvania 15260, USA

**Devendra Kumar** (Chapter 8)

Department of Applied Chemistry  
Delhi College of Engineering  
University of Delhi  
Bawana Road  
Delhi 110042, India

**Dongdong Li** (Chapter 2)

Department of Physics and Department of Electrical Engineering  
University of Southern California  
Los Angeles, California 90089-0484, USA

**Jia Grace Lu** (Chapter 2)

Department of Physics and Department of Electrical Engineering  
University of Southern California  
Los Angeles, California 90089-0484, USA

**Ralf Moos** (Chapter 7)

Department of Functional Materials  
University of Bayreuth  
95440 Bayreuth, Germany

**Rajesh** (Chapter 8)

Liquid Crystal and Self Assembled Monolayer Section  
National Physical Laboratory (CSIR)  
Dr. K.S. Krishnan Marg  
New Delhi 110012, India

**Kathy Sahner** (Chapter 7)

Functional Materials Laboratory  
University of Bayreuth  
95440 Bayreuth, Germany

**Alexander Star** (Chapter 3)

Department of Chemistry  
University of Pittsburgh and the National Energy Technology Laboratory  
Pittsburgh, Pennsylvania 15260, USA

**Michael Tiemann** (Chapter 6)

Department of Chemistry

Faculty of Science

University of Paderborn

Warburger Strasse 100

D-33098 Paderborn, Germany

**Ulrike Tisch** (Chapter 4)

Department of Chemical Engineering

Technion—Israel Institute of Technology

Haifa 32000, Israel

# 目 录

<b>5 多孔半导体材料及用于气体传感器的优缺点</b>	<b>1</b>
1 引 言	1
2 多孔半导体：制备原理与特性	3
3 基于多孔半导体的气体传感器——方法和特点	24
4 应用于微加工传感器技术中的多孔硅的优点	67
5 展 望	72
6 致 谢	74
参考文献	74
 <b>6 有序介孔膜的合成、性质及其在气体传感器中的应用</b>	 <b>89</b>
1 引 言	89
2 电阻式气体传感器的孔隙度	90
3 合成方法	95
4 总 结	101
参考文献	102
 <b>7 以沸石为基本材料的化学传感器</b>	 <b>109</b>
1 引 言	109
2 沸石——特性及应用	110
3 沸石作为化学传感器中的辅助相	114

4 沸石作为功能(敏感)相 .....	120
5 结 论 .....	126
参考文献 .....	126
<b>8 纳米复合材料的制备及其在化学传感器中的应用 .....</b>	<b>133</b>
1 引 言 .....	133
2 纳米复合材料的类型 .....	135
3 纳米复合材料制备的一般方法 .....	136
4 金属氧化物基纳米复合材料 .....	137
5 聚合物基纳米复合材料 .....	142
6 碳纳米管基纳米复合材料 .....	147
7 贵金属基纳米复合材料 .....	153
8 展 望 .....	159
9 致 谢 .....	159
参考文献 .....	160
<b>索 引 .....</b>	<b>167</b>
<b>丛书书目</b>	

# CONTENTS

<b>5</b>	<b>POROUS SEMICONDUCTORS: ADVANTAGES AND DISADVANTAGES FOR GAS SENSOR APPLICATIONS</b>	<b>203</b>
	<i>G. Korotcenkov</i>	
1	Introduction	203
2	Porous Semiconductors: Principles of Fabrication and Properties	205
2.1	Principles of Porous Silicon Fabrication	205
2.2	Properties of Porous Silicon	208
2.3	Techniques for Forming the Porous Silicon Layer	210
2.4	Porosification of Standard Semiconductors	220
3	Gas Sensors Based on Porous Semiconductors—Approaches and Characteristics	226
3.1	Capacitance-Type Gas Sensors	226
3.2	Gas Sensors Employing Photoluminescence Quenching	232
3.3	Sensors Based on Optical Measurements	237
3.4	Conductometric-Type Gas Sensors	243
3.5	Gas Sensors Based on Schottky Barriers and Heterostructures	250
3.6	Gas Sensors Based on Measurement of Contact Potential Difference	257
3.7	Gas Sensors Based on Simultaneous Control of Several Parameters of the Porous Material	258
3.8	Disadvantages of Porous Semiconductor Gas Sensors	259
3.9	Surface Modification of Porous Semiconductors to Improve Gas-Sensing Characteristics	265
4	Advantages of Porous Silicon for Applications in Micromachining Sensor Technology	269
5	Outlook	274
6	Acknowledgments	276
	References	276

<b>6</b>	<b>ORDERED MESOPOROUS FILMS AND MEMBRANES: SYNTHESIS, PROPERTIES, AND APPLICATIONS IN GAS SENSORS</b>	<b>291</b>
	<i>M. Tiemann</i>	
1	Introduction	291
2	Porosity in Resistive Gas Sensors	292
2.1	Categories of Porosity	292
2.2	Gas Diffusion in Porous Materials	293
2.3	Porous Films for Selective Gas Sensing	293
2.4	Other Porosity-Related Nanostructural Aspects	296
3	Synthesis Methods	297
3.1	Mesoporous Metal Oxides by Conventional Synthesis Methods	297
3.2	Mesoporous Materials by Supramolecular Structure Directors	299
3.3	Mesoporous Materials by Structure Replication	302
4	Summary	303
	References	304
<b>7</b>	<b>CHEMICAL SENSORS BASED ON ZEOLITES</b>	<b>311</b>
	<i>R. Moos</i>	
	<i>K. Sahner</i>	
1	Introduction	311
2	Zeolites—Properties and Applications	312
3	Zeolites as an Auxiliary Phase in Chemical Sensors	316
3.1	Zeolites as Host Materials	316
3.2	Zeolites as Filters	319
3.3	Zeolites as Preconcentrators	321
3.4	Zeolites as Templates	321
4	Zeolites as the Functional (Sensitive) Phase	322
4.1	Adsorptivity	322
4.2	Ionic Conductivity	323
4.3	Catalytic Activity	326
5	Conclusion	328
	References	328



<b>8 NANOCOMPOSITES: FROM FABRICATION TO CHEMICAL SENSOR APPLICATIONS</b>	<b>335</b>
<i>Rajesh</i>	
<i>T. Ahuja</i>	
<i>D. Kumar</i>	
1 Introduction	335
2 Types of Nanocomposites	337
3 General Approaches to Nanocomposite Fabrication	338
4 Metal Oxide–Based Nanocomposites	339
4.1 Synthesis	339
4.2 Properties	340
4.3 Application in Chemical Sensors	341
5 Polymer-Based Nanocomposites	344
5.1 Synthesis	344
5.2 Properties	346
5.3 Application in Chemical Sensors	347
6 Carbon Nanotube–Based Nanocomposites	349
6.1 Synthesis	350
6.2 Properties	352
6.3 Application in Chemical Sensors	353
7 Noble Metal–Based Nanocomposites	355
7.1 Synthesis	357
7.2 Properties	358
7.3 Application in Chemical Sensors	359
8 Outlook	361
9 Acknowledgment	361
References	362

## INDEX

## SERIES CATALOG