国家出版基金项目
NATIONAL PUBLICATION FOUNDATION

有色金属理论与技术前沿丛书
SERIES OF THEORETICAL AND TECHNOLOGICAL FRONTIERS OF NONFERROUS METALS

# 中空结构无机功能材料

# INORGANIC FUNCTIONAL MATERIALS WITH HOLLOW INTERIORS

刘小鹤 马仁志 李星国 著
Liu Xiaohe Ma Renzhi Li Xingguo

中南大学出版社
www.csupress.com.cn
CNMC 中国有色集团

国家出版基金项目
NATIONAL PUBLICATION FOUNDATION

有色金属理论与技术前沿丛书

# 中空结构无机功能材料

INORGANIC FUNCTIONAL MATERIALS WITH HOLLOW INTERIORS

刘小鹤　马仁志　李星国　著
Liu Xiaohe　Ma Renzhi　Li Xingguo



中南大学出版社
www.csupress.com.cn
中国有色集团

**图书在版编目(CIP)数据**

中空结构无机功能材料/刘小鹤,马仁志,李星国著.
—长沙:中南大学出版社,2015.7
ISBN 978-7-5487-1740-9

Ⅰ.中... Ⅱ.①刘...②马...③李... Ⅲ.中空纤维-纳米材料-无机材料-功能材料 Ⅳ.TB321

中国版本图书馆 CIP 数据核字(2015)第 159791

**中空结构无机功能材料**

刘小鹤 马仁志 李星国 著

□**责任编辑** 刘颖维
□**责任印制** 易建国
□**出版发行** 中南大学出版社
社址:长沙市麓山南路 邮编:410083
发行科电话:0731-88876770 传真:0731-88710482
□**印 装** 长沙超峰印务有限公司

□**开 本** 720×1000 1/16 □**印张** 24 □**字数** 477 千字
□**版 次** 2015 年 7 月第 1 版 □**印次** 2015 年 7 月第 1 次印刷
□**书 号** ISBN 978-7-5487-1740-9
□**定 价** 115.00 元

# Introduction

This book aims to present some recent advances in the exciting research field of inorganic functional materials with hollow interiors as well as the insight into the morphological and structural evolution among them. We have selected our related publications dedicated to the subject covering layered hydroxide and oxide nanocones, inorganic nanotubes, cobalt and nickel oxide nanorings, rare-earth oxide and oxysulfate hollow spheres, transition-metal oxide and chalcogenides hollow spheres, ferrite and metallic and polypyrrole hollow spheres. It surely will be a great relief and pleasure for us if this book provides a candid glimpse to the active and exciting research area of inorganic functional materials with hollow interiors. We sincerely hope that this book may be available for reference to established scientists and scholars.

# About the Authors

**Liu Xiaohe** received his Ph. D from the Central South University in 2005, Changsha. He became an Associate Professor and then Full Professor at the School of Resources Processing and Bioengineering of Central South University in 2007 and 2012, and distinguished professor of the Shenghua Scholar Program of Central South University in 2011. He joined the School of Materials Science and Engineering of Central South University in 2014. His research interests focus on, layer-structured materials, novel unilamellar nanosheets, and hollow structure of nanomaterials, as well as darifying the close relationship between the microstructure of as-prepared products and their properties. He has already published more than 70 papers in SCI journals, such as *Advance Materials*, *Angewandte Chemie International Editon*, *ACS Nano*, *Advanced Functional Materials*, *Journal of the American Chemical Society*, etc. which have been cited more than 1600 times, and H-index has reached 26. He has received Hunan Province Natural Science Award (2010) and Outstanding Youth Fund in Hunan Province (2013).

**Ma Renzhi** received his B. S. and Ph. D both from Tsinghua University in 1995 and 2000, Beijing. He has been a principal researcher at the National Institute for Material Science (Japan). He joined the School of Materials Science and Engineering of Central South University in 2014. He has accomplished a series of international cutting-edge research work, especially the systematic research on the intercalation/exfoliation chemistry of inorganic layered compounds, single-layer nanosheets and hollow structure of nanomaterials. He has already published more than 130 papers and have been cited for more than 7000 times. The H-index of his citations is 45. He co-holds 22 authorized Japan patents. He was selected as an Innovative Talent offered by Recruitment Program of Global Experts (One-Thousand-Talents Plan) in China. He received 2009 Award for Distinguished Lectureship at Asian International Forum for Young Scientists of the Chemical Society of Japan, and "Chemical Physics Letter" 2003—2007 Most Cited Paper Award.

**Li Xingguo** received his Ph. D from Tohoku university in 1990, Japan. He is the Professor and Director of New Energy and Nano Materials Laboratory, Chairman of the Inorganic Chemistry Institute at Peking University. He is also a Guest Professor of Hiroshima University (Japan). He is an editor for the *Chinese Journal of Inorganic Materials*, *the Chinese Journal of Inorganic Chemistry*, *the Chinese Journal of Process Engineering*, *Journal of Chinese Rare Earth Society*, *Journal of Rare Earth*, *Journal of Applied Chemistry and the Chinese Journal of Functional Materials*. His research interests focus on hydrogen storage materials, hydrogen generation and purification, battery electrode materials and nano materials. He has already published more than 250 papers and contributed chapters to three books published by Nova Science Publishers, Inc. and American Scientific Publishers. He has received the National Distinguished Young Investigator Fund (2000), Lectureship Award of Japan Research Institute of Material Technology (2002) and GM Foundation Science & Technology Achievement Award (2005).

# Academic Committee

National Publication Foundation / Series of Theoretical and Technological Frontiers of Nonferrous Metals

# Preface

Nowadays, nonferrous metals have become the important material basis for the development of national economic, science and technology, national defense and so on, and are the key strategic resources for enhancing the comprehensive national strength and national security. As a nonferrous metals production superpower, the nonferrous metals research field in China has made great progress, particularly in the development and utilization of complex and low-grade nonferrous metals resources.

The nonferrous metals industry in China has developed rapidly in the recent 30 years. The production has been the maximal in the world year after year. The science and technology of nonferrous metals is playing an increasingly important role in the national economic construction and the modernization of national defense. At the same time, the contradiction between the shortage of nonferrous metals resources and the economic development is increasingly serious. The dependence on foreign resources has been increasing year by year, which seriously affects the healthy development of our national economy.

With the economic development, high-quality mineral resources have proven to be nearly depleted. This makes China face the crisis of critical shortage of the total supply of nonferrous metals. Furthermore, when the complex and low-grade mineral resources or secondery raw materials, which have the characteristics of difficult exploration, difficult mining, difficult processing and difficult metallurgy, gradually become the main resources, a huge challenge will be exerted on the traditional science and technology, such as geology, mining,

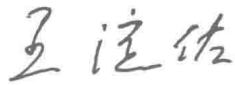
mineral processing, metallurgy, materials, processing, and enviroment. The nonferrous metals industry and related industries are facing the competition for the survival of the crisis due to low-quality resources. The development of nonferrous metals industry urgently needs new theories and new technologies to adapt to the characteristics of the resources. The publication of nonferrous metals books that own complete system, leading level and mutual integration will improve the independent innovation ability of the nonferrous metals industry and promote the application of new theories and new technologies of high-efficiency, low consumption, non-pollution and comprehensive utilization of the nonferrous metals resources. It will play a vital role in ensuring the sustainable development of the nonferrous metals industry in China.

As a major national publication project, the *Series of Theoretical and Technological Frontiers of Nonferrous Metals* plan to publish 100 kinds of books, which cover materials, metallurgy, mining, earth science, mechanical and electrical engineering and so on. The authors of these books include academicians who work in the field of nonferrous metals, chief scientists of major national research projects, Yangtze River Scholars, winners of China National Funds for Distinguished Young Scientists, winners of the National Excellent Doctoral Dissertation, talented persons selected by major national talent programs, leading experts in large-scale research institutes of nonferrous metals and key enterprises.

The National Publication Foundation established by the state is to encourage and support the publication of outstanding public service works that represent the highest level of the national academic publication. The *Series of Theoretical and Technological Frontiers of Nonferrous Metals* will aim at the frontiers of nonferrous metals and grasp the latest development of nonferrous metals at home and abroad. They will comprehensively, promptly and accurately reflect the new

theories, new technologies and new applications of nonferrous metals, and explore and capture the highly valuable research achievements, thus owning high academic values.

The Central South University Press has devoted long-term effort to publishing books of nonferrous metals. A lot of very effective work has been done in the course of publishing the *Series of Theoretical and Technological Frontiers of Nonferrous Metals*. This will vigorously promote the publication of outstanding scientific and technological works in the nonferrous metals industry, and play a direct and significant role in cultivating personnel of the nonferrous metals disciplines in the universities, research institutes and enterprises of China.



**Wang Dianzuo**

**Dec 2010**

# Foreword

This book aims to present some recent advances in the exciting research field of nanotubes, especially the designed synthesis of various functional materials with hollow interiors as well as the insight into the morphological and structural evolution among them. It is generally believed that, for any inorganic functional material with a layered structure, nanotubes could be formed under appropriate conditions ( chemical vapor deposition, hydrothermal synthesis, etc. ). In fact, many kinds of inorganic nanotubes made of carbon, boron nitride ( BN ), transition-metal halides, oxides, and chalcogenides, all possessing natural or artificial layered structures, have successfully been produced based on a "rolling-up" mechanism, analogous to a paper scroll.

Compared with the layered counterparts, the formation of nanotubes from nonlayered materials requires much more effort to assemble atoms or small particles into a tubular structure during crystallization. As a result, the preparation of nanotubes from nonlayered materials is often subjected to the use of sacrificial templates such as nanotubes, nanowires, nanorods, and porous membranes. Although the sacrificial templating method has been proved to be a facile and efficient approach for the growth of tubular structures, sometimes the final product might be disrupted during the templates removing processes.

In addition to cylindrical nanotubes, layered materials might be able to form conical structures with hollow interiors by the same

rolling-up mechanism. Derived from the peculiar conical feature, nanocones exhibit special electronic, mechanical, and field-emission properties. However, apart from carbon and boron nitride systems, there are few reports focusing on conical structures originating from the rolling-up of layered materials. On the other hand, a large variety of layered materials could be exfoliated/delaminated into single-layer nanosheets by controlling layer-to-layer interaction through soft chemical procedures. Even nanotubes can be unwrapped/unravelled into individual sheets under a similar scenario. For example, carbon nanotubes could be unzipped/exfoliated to fabricate graphene sheets or ribbons. In general, layered oxide and hydroxide crystals adopt a lamellar or plate-like morphology. The question arises as to, besides carbon and boron nitride (BN), whether conical structures can be formed by the rolling-up of layered oxides and hydroxides, and if the nanocones can be further unwrapped/exfoliated into single-layer nanosheets. The pursuit of the answer to this intriguing question will be very important in revealing the formation mechanism of nanocones as well as the energy balance between nanocones and nanosheets.

Another interesting morphology for inorganic materials, hollow spheres with nanometer or micrometer dimensions, are attractive in various fields, such as controlled release capsules, artificial cells, selective catalysis, chemical storage and sensors, photonic crystals, biomedical diagnosis and therapy. Numerous chemical and physicochemical strategies such as the kirkendall diffusion effect, spray pyrolysis, ostwald ripening, template-assisted synthesis and chemically induced self-transformation have been employed for the design and controlled fabrication of various micro/nanospheres with hollow interiors. Traditionally, template-assisted synthetic strategies including hard and soft templates have been demonstrated to be the most effective and versatile approach. In this regard, various templates, such as hard ones (e. g., silica, polymer, and carbon