# Functional Nanomaterials

## A Chemistry and Engineering Perspective

## 纳米功能材料

*Edited by*

Shaowei Chen

Wenbin Lin

陈少伟 林文斌 主编

University of Science and
Technology of China Press

中国科学技术大学出版社

当代科学技术基础理论与前沿问题研究丛书

中国科学技术大学

# 校友文库

# Functional Nanomaterials

## A Chemistry and Engineering Perspective

## 纳米功能材料

*Edited by*

Shaowei Chen

Wenbin Lin

陈少伟 林文斌 主编

University of Science and
Technology of China Press

中国科学技术大学出版社

## 内 容 简 介

纳米结构材料的研究与应用广泛存在于多个领域，包括化学、物理、生命科学与工程科学等。本书试图从纳米功能材料的化学与工程性能入手，探索材料尺寸影响材料性质功能的微观机理，并通过一些具体实例说明这些独特的材料性能在不同领域的应用。本书包括4个部分。第1部分（第1至5章）介绍了多种纳米功能材料（如纳米线、纳米颗粒）的制备、处理、功能化与表征。材料制备是实现材料应用的一个重要环节。第2部分（第6到10章）侧重于纳米材料的电子转移性能以及在纳米电子器件和分子电子器件上的重要性。第3部分（第11到13章）总结了近年来纳米功能材料在能源研究上的一些进展（如太阳能、燃料电池）。第4部分（第14到16章）介绍纳米材料在生物标定、检测和敏感器件中的应用。

本书可作为从事纳米材料及其相关领域科研人员的技术参考资料，也可以作为高年级本科生和研究生相关课程的辅助读物。

**Functional Nanomaterials: A Chemistry and Engineering Perspective**
Edited by Shaowei Chen & Wenbin Lin

Published by University of Science and Technology of China Press
96 Jinzhai Road, Hefei 230026, P. R. China

**图书在版编目(CIP)数据**

纳米功能材料 = Functional Nanomaterials: A Chemistry and Engineering Perspective: 英文/陈少伟，林文斌主编. —合肥：中国科学技术大学出版社，2009.4
（当代科学技术基础理论与前沿问题研究丛书：中国科学技术大学校友文库）
“十一五”国家重点图书
ISBN 978-7-312-02269-2

Ⅰ.纳… Ⅱ.①陈…②林… Ⅲ.纳米材料：功能材料—英文 Ⅳ.TB383

中国版本图书馆 CIP 数据核字(2008)第126188号

中国科学技术大学出版社出版发行
地址：安徽省合肥市金寨路96号，230026
网址：http://press.ustc.edu.cn
合肥晓星印刷有限责任公司印刷
全国新华书店经销

开本：710×1000 1/16 印张：39.75 插页：1 字数：650千
2009年4月第1版 2009年4月第1次印刷
印数：1—1500册
定价：118.00元

# 总　　序

侯建国
（中国科学技术大学校长、中国科学院院士、第三世界科学院院士）

大学最重要的功能是向社会输送人才。大学对于一个国家、民族乃至世界的重要性和贡献度，很大程度上是通过毕业生在社会各领域所取得的成就来体现的。

中国科学技术大学建校只有短短的50年，之所以迅速成为享有较高国际声誉的著名大学之一，主要就是因为她培养出了一大批德才兼备的优秀毕业生。他们志向高远、基础扎实、综合素质高、创新能力强，在国内外科技、经济、教育等领域做出了杰出的贡献，为中国科大赢得了"科技英才的摇篮"的美誉。

2008年9月，胡锦涛总书记为中国科大建校五十周年发来贺信，信中称赞说：半个世纪以来，中国科学技术大学依托中国科学院，按照全院办校、所系结合的方针，弘扬红专并进、理实交融的校风，努力推进教学和科研工作的改革创新，为党和国家培养了一大批科技人才，取得了一系列具有世界先进水平的原创性科技成果，为推动我国科教事业发展和社会主义现代化建设做出了重要贡献。

据统计，中国科大迄今已毕业的5万人中，已有42人当选中国科学院和中国工程院院士，是同期（自1963年以来）毕业生中当选院士数最多的高校之一。其中，本科毕业生中平均每1000人就产生1名院士和700多名硕士、博士，比例位居全国高校之首。还有众多的中青年才俊成为我国科技、企业、教育等领域的领军人物和骨干。在历年评选的"中国青年五四奖章"获得者中，作为科技界、科技创新型企业界青年才俊代表，科大毕业生已连续多年榜上有名，获奖总人数位居全国高校前列。鲜为人知的是，有数千名优秀毕业生踏上国防战线，为科技强军做出了重要贡献，涌现出20多名科技将军和一

大批国防科技中坚。

为反映中国科大五十年来人才培养成果，展示毕业生在科学研究中的最新进展，学校决定在建校五十周年之际，编辑出版《中国科学技术大学校友文库》，于2008年9月起陆续出书，校庆年内集中出版50种。该《文库》选题经过多轮严格的评审和论证，入选书稿学术水平高，已列为国家“十一五”重点图书出版规划。

入选作者中，有北京初创时期的毕业生，也有意气风发的少年班毕业生；有“两院”院士，也有IEEE Fellow；有海内外科研院所、大专院校的教授，也有金融、IT行业的英才；有默默奉献、矢志报国的科技将军，也有在国际前沿奋力拼搏的科研将才；有“文革”后留美学者中第一位担任美国大学系主任的青年教授，也有首批获得新中国博士学位的中年学者；……在母校五十周年华诞之际，他们通过著书立说的独特方式，向母校献礼，其深情厚意，令人感佩！

近年来，学校组织了一系列关于中国科大办学成就、经验、理念和优良传统的总结与讨论。通过总结与讨论，使我们更清醒地认识到，中国科大这所新中国亲手创办的新型理工科大学所肩负的历史使命和责任。我想，中国科大的创办与发展，首要的目标就是围绕国家战略需求，培养造就世界一流科学家和科技领军人才。五十年来，我们一直遵循这一目标定位，有效地探索了科教紧密结合、培养创新人才的成功之路，取得了令人瞩目的成就，也受到社会各界的广泛赞誉。

成绩属于过去，辉煌须待开创。在未来的发展中，我们依然要牢牢把握“育人是大学第一要务”的宗旨，在坚守优良传统的基础上，不断改革创新，提高教育教学质量，早日实现胡锦涛总书记对中国科大的期待：瞄准世界科技前沿，服务国家发展战略，创造性地做好教学和科研工作，努力办成世界一流的研究型大学，培养造就更多更好的创新人才，为夺取全面建设小康社会新胜利、开创中国特色社会主义事业新局面贡献更大力量。

是为序。

2008年9月

# Preface

2008 is a special year for many of us. Fifty years ago, the University of Science and Technology of China (USTC) was established in Beijing, China under the auspice of the Chinese Academy of Sciences. Despite the relatively short history in higher education, USTC has distinguished herself with tens of thousands of outstanding alumni who have been making significant contributions to the nation and to the world as a whole by advancing the forefronts of science and technology. As part of the festivities this year to celebrate the half-century mark of the university, a group of young proud alumni, most of whom attended USTC in the 1980s and 1990s and are currently holding tenured/tenure-track faculty positions in the USA, have decided to showcase their talents and accomplishments in the fields of nanoscience and nanotechnology, and hence the birth of this book as a token of appreciation of the unparalleled undergraduate education that they received from the alma mater.

The theme of this book is focused on the chemistry and engineering aspects of nanoscale functional materials. The extensive interest in nanostructured materials is primarily motivated by the chemical and physical properties that are inaccessible in either their constituent atoms/molecules or bulk forms. As exemplified in this book, diverse applications have been proposed and pursued in multiple disciplines, ranging from materials chemistry, physics, to biology and engineering. Therefore, in this book, the chapters are divided into four major groups to address these different issues. Part Ⅰ (Chapters 1 – 5) focuses on the synthesis and manipulation of varied nanostructured materials. The fundamental insights that we gain about the mechanistic growth and chemical transformation are anticipated to lay the foundation for rational designs of nanomaterials with specific functionalities. Part Ⅱ (Chapters 6 – 10) covers the unique electron transfer/transport properties of nanostructured materials and their implication in nanoelectronics and molecular electronics. In fact, this is one of the major driving forces in nanomaterials research in that potential new technologies may be developed to complement or even surpass the current silicon-based semiconductor technology. Part Ⅲ (Chapters 11 - 13) reviews some of the recent progress in the applications of functional nanomaterials in energy science and engineering (solar cells and fuel cells); and last but not least, Part Ⅳ (Chapters 14 - 16) surveys the applications of nanomaterials in biological labeling, biomedical imaging, and sensing and detection in biomolecules.

As editors of this book project, we are grateful to the fellow alumni who took time out of their hectic schedules to contribute to the book. We are overwhelmed by the enthusiastic and unconditional support from a wide range of alumni, from seasoned pioneers in the fields to brand-new but energetic assistant professors. It is thus our sincere hope that this book will provide a glimpse of the many facets of distinctions of the proud alumni of USTC. In addition, the book is intended to offer a timely survey of the state of the art of nanoscience and nanotechnology, and thus may serve as a technical reference to researchers interested in nanomaterials science and engineering.

Happy 50th Anniversary, Alma Mater!

Shaowei Chen
陈少伟 (8603)
*Santa Cruz, California*

Wenbin Lin
林文斌 (8303)
*Chapel Hill, North Carolina*

# Contents

# Part I

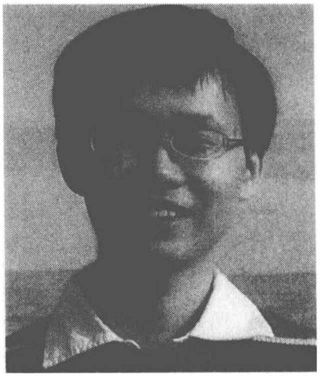
# Nanomaterial Chemistry

# *Chapter 1*

# Shape-Controlled Synthesis of Palladium Nanostructures

Yujie Xiong① and Younan Xia * ②

**Yujie Xiong** was born in Jiangxi, China, in 1979. He entered the Special Class for the Gifted Youth (SCGY) at the University of Science and Technology of China (USTC) in 1996, received a B. S. degree in chemical physics in 2000, and a Ph. D. degree in inorganic chemistry in 2004 (with Prof. Yi Xie). He is the recipient of a number of prestigious awards during the course of his graduate study, including the Best Doctoral Thesis Award from the Chinese Academy of Sciences. From 2004 to 2007, he worked as a postdoctoral fellow with Prof. Younan Xia at the University of Washington in Seattle, where his research centered on shape-controlled synthesis and property tailoring of metal nanostructures. He is currently working with Prof. John A. Rogers at the University of Illinois at Urbana-Champaign. His research interests include micro- and nanofabrication, electronic and photonic devices, synthesis and self-assembly of inorganic nanostructures, nucleation and growth, surface plasmon resonance, and surface-enhanced Raman scattering (SERS). He has published more than 50 papers and book chapters.



**Younan Xia** was born in Jiangsu, China, in 1965. He received a B.S. degree in chemical physics from the University of Science and Technology of China (USTC) in 1987 and then worked as a graduate student on nonlinear optical materials for 4 years at the Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. He came to the United States in 1991, received a M.S. degree in inorganic chemistry from University of Pennsylvania (with Professor Alan G. MacDiarmid) in 1993, and a Ph. D. degree in physical chemistry from Harvard University (with Professor George M. Whitesides) in 1996. He then worked as a postdoctoral

---

① Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Illinois 60181, USA.

② Department of Biomedical Engineering Washington University, St. Louis, Missouri 63130, USA.

* Corresponding author. E-mail: xia@biomed.wustl.edu.

fellow with Professors George M. Whitesides and Mara Prentiss. He moved to Seattle in 1997 and started as an Assistant Professor of Chemistry at the University of Washington. He was promoted to the rank of Professor in 2004. He moved to the Department of Biomedical Engineering at Washington University in St. Louis in September 2007, and is currently the James McKelvey Professor for Advanced Materials. His research interests include nanostructured materials, nanomedicine, biomaterials, self-assembly, photonic crystals, colloidal science, microfabrication, surface patterning, and electrospinning.

# 1 Introduction

In 1959, Richard Feynman, a Nobel Laureate suggested in his famous lecture entitled 'There's Plenty of Room at the Bottom' that many physical measurements could be pushed to very small scales to reveal new phenomena and obtain new applications. Half a century later, Feynman's vision has become the foremost frontier of scientific research, with the establishment of a new field known as nanotechnology. This field involves manipulation and investigation of structures with at least one dimension in the range of 1 to 100 nm. A central theme of research in this field is to fabricate or grow nanostructures from their constituent atoms with controllable sizes, shapes, compositions, and properties.

Among various systems, metal nanostructures have received intensive attention over the past decades, as metals cover almost two thirds of elements in the period table. Metal nanostructures have a broad range of fascinating properties, many of which have found extensive use in various applications including optical sensing/imaging, biomedicine, photography, information storage, ferrofluids, heterogeneous catalysis, electronics, and photonics.[1-6] However, it has been a long-term challenge to precisely tailor and control their properties for different applications. Like their semiconductor counterparts, the properties of metal nanostructures are highly dependent on the size, shape, composition, crystallinity, and structure (e.g., solid versus hollow). One can, in principle, adjust any one of these parameters to control their properties. Most recently, the focus of research has been shifted to shape control partly because in many cases it allows one to tune the properties with a greater versatility than can be achieved otherwise. A notable example is related to surface plasmon resonance (SPR). It has been predicted by calculations that both the number and position of SPR peaks of Ag or Au nanostructures, as well as their effective spectral range for surface-enhanced Raman scattering (SERS), are highly sensitive to the shape of nanostructures.[7] This shape dependence has also been verified by a number of experimental studies. For instance, the longitudinal SPR modes of Ag and Au nanorods have been shown to drastically red-shift from the visible to the nearinfrared with increasing aspect ratio;[2c] arrayed Ag triangular nanoparticles have been demonstrated as effective substrates for SERS in the spectral range from 700 to 800 nm, while the most suitable SERS spectral range for spherical Ag nanoparticles is between 530 and 570 nm.[6d, 8] In catalysis, shape control has enabled people to improve the activity and selectivity of metal nanoparticles for a rich variety of reactions. For example, Pt nanocubes whose surfaces are enclosed by {100} facets catalyze reactions involving hydrogen efficiently, while the reactivity of carbon monoxide can be enhanced by the {210} facets of buckyball-shaped nanoparticles.[9,10]

We have been engaged in the development of facile methods for shape-controlled synthesis of metal nanostructures. In this chapter, we will take palladium as an example to demonstrate a variety of useful parameters that can be tuned to control the formation of metal nanostructures with a specific shape in a solution-phase synthesis. We are interested in palladium because this noble metal plays a central role in many industrial applications.[11-13] It serves as the primary catalyst for the low-temperature reduction of automobile pollutants,[11] as well as a range of organic reactions that include Suzuki, Heck, and Stille couplings.[12] It also has remarkable performance in hydrogen storage and sensing.[13] Essentially, all of these applications require the use of palladium in a finely divided state where both the size and shape are critical parameters to control in order to maximize their values. Shape control can have a huge impact on these applications. For example, the reactivity and selectivity of a Pd nanocatalyst can be tailored by controlling the shape as it will determine the crystallographic facets exposed on the surface of a nanocrystal and therefore the number of atoms located at the edges or corners.[14] Another useful property of palladium that remains largely unexplored is the SPR.[15] Calculations based on the discrete dipole approximation (DDA) method have indicated that the resonance peaks of Pd nanostructures could be tuned from the ultraviolet (330 nm) to the visible (530 nm) region by tailoring their shape from cube to icosahedron and then triangular thin plate without any change on the edge length.[16] Since the resonance peaks are close to the wavelengths of lasers commonly used for Raman spectroscopy, both Pd icosahedrons and thin plates can serve as substrates for SERS detection with greatly improved activities.[17]

Like other noble metals, synthesis of Pd nanostructures with well-controlled shapes has been a challenging task. Before we started to work on this subject, a lot of efforts had been devoted to the chemical synthesis of Pd nanostructures, including the use of surfactants, polymers, or RNAs to mediate the reaction; the use of a coordinating ligand to direct the growth; as well as the decomposition of a specially designed Pd-surfactant complex.[18] The control knobs available for these syntheses have been limited to the reaction temperature, the concentration of Pd precursor, and the structure of the surfactant or polymer. The products that can be obtained using these methods are typically cuboctahedrons, thin plates, and irregularly shaped particles. In order to systematically study the shape-property relationship and fully explore their potential applications, it is necessary to develop a generic approach to Pd nanostructures with a broad range of well-defined shapes.

As a face-centered cubic (*fcc*) metal, Pd nanostructures can take a variety of geometrical shapes.[19] Our recent work on the Ag system indicates that the crystallinity of seeds plays the most important role in controlling the shape of final products.[20] Due to their similar crystal structures, we believe that maneuvering the crystallinity of Pd seeds also holds the key to the shape control of Pd nanostructures. Further growth of seeds may selectively enlarge one set of crystallographic facets at the expense of others to yield the final shape. As a result, it is feasible to determine which facet will be exposed on the surface and thus the final shape by controlling the growth rates of different facets. Along this line, we and other groups have started to attack a long-standing problem in chemistry and physics — understanding and control of both nucleation and growth details involved in the chemical synthesis of nanostructures. As the focus of this chapter, we will discuss how a precise control over nucleation and growth can be achieved in a solution-phase synthesis by tuning a number of critical parameters. The ultimate goal of our research is to provide an atomistic picture of the evolution pathway from atoms to clusters and nanostructures, as well as the design rules for synthesizing metal nanostructures with well-controlled electronic, magnetic, catalytic and optical properties.

## 2 Nucleation and Growth

In a typical solution-phase synthesis of metal nanostructures, the very