One-Dimensional Nanostructures

Concepts, Applications and Perspectives

一维纳米结构材料

概念、应用和展望

Edited by

Yong Zhou

周 勇 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
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内 容 简 介

纳米材料是20世纪80年代中期一个迅速发展的材料科学领域，受到人们广泛的关注。本书选择性的汇集了国内外中国科技大学校友在一维纳米材料的最新科技研究成果。书中介绍了一维纳米材料包括纳米线、纳米管和纳米带等当今研究的趋势、相关技术与未来发展方向，是化学、物理和材料等学科的基础理论研究与应用技术的前沿集成反映。

本书适合于高等学校、科研院所以及相关企业从事纳米材料研发的科研人员和管理工作者，同时也可作为相关专业的师生和爱好者学习参考用书。

图书在版编目(CIP)数据

一维纳米结构材料：概念、应用和展望＝One-Dimensional Nanostructures：Concepts，Applications and Perspecticves：英文/周勇主编. —合肥. 中国科学技术大学出版社，2009. 7

（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 978-7-312-02201-2

Ⅰ. 一… Ⅱ. 周… Ⅲ. 纳米材料—研究—英文 Ⅳ. TB383

中国版本图书馆CIP数据核字(2008)第151958号

出版发行 中国科学技术大学出版社

地址 安徽省合肥市金寨路96号，230026

网址 http://press.ustc.edu.cn

印　　刷 合肥晓星印刷有限责任公司

经　　销 全国新华书店

开　　本 710mm×1000mm 1/16

插　　页 1

印　　张 17.75

字　　数 303千

版　　次 2009年7月第1版

印　　次 2009年7月第1次印刷

定　　价 58.00元

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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五十年，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名院士和七百多名硕士、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。

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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，涌现出二十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"十一五"国家重点图书出版规划。

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，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

It is my great honor to put together this book to celebrate the 50th anniversary of University of Science and Technology of China (USTC). Nanotechnology has been revolutionalizing daily life in the last two decades. Tremendous progress in one-dimensional (1-D) nanostructures including nanowires, nanotubes and nanoribbons has been seen in recent years. It is considered timely to provide a survey of a number of important developments in this field. To this end, *One-Dimensional Nanostructures: Concepts, Applications and Perspectives* combines contributions from fabrication and application of 1-D nanostructures in an attempt to give the reader a feel for the scope of current and potential future developments. Although the book is not the intention to be comprehensive, specific research topics are selected that reflects the fascinating possibilities offered by 1-D nanostructures.

Because there are so many researchers in this rapidly growing field, I have only invited 8 alumni specialists of the USTC in the representative areas to contribute to this special book. In chapter 1, Zhou reviews the formation and application of lipid nanotubes and peptide nanotubes. In chapter 2, Lao and coworkers give a comprehensive introduction of nanodevices based on ZnO nanowires/nanobelts and the most recent research progress in this area. Hu illustrates elastic properties of 1-D metal nanoparticles studied by time-resolved spectroscopy in chapter 3. Zhu reviews the main research work regarding the microwave-assisted rapid preparation of 1-D nanostructures in chapter 4. Chapter 5 by Xiong et al surveys recent developments in the solution-phase synthesis of one-dimensional inorganic nanostruetures. Shen and coworkers describe in chapter 6 focused on 1-D nanoscale heterostructures, especially on the synthesis of 1-D nanoscale heterostmctures

using the vapor related processes. In chapter 7, Deng and coworkers introduce recent developments in DNA nanotechnology-based strategies for 1-D nanostructure fabrications. In chapter 8, Xu reports the synthesis of rare earth compound 1-D nanostructures, template-directed synthesis of 1-D nanostructures, biomimetic synthesis of 1-D nanostructures, other functional 1-D nanostructures, and the formation mechanism of 1-D nanostructures by soft chemistry routes.

In the edition of this book I am indebted to Prof. Zuyao Chen (Department of Chemistry, USTC) for his great support. I am also extremely grateful to the authors for their excellent contributions. I hope that this book will be a source of inspiration for many researchers and stimulate new developments in this challenging field of science.

Happy Birthday, USTC!

Yong Zhou
Nanjing, China, 2009

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Chapter 1

Lipid Nanotubes and Peptide Nanotubes: Formation and Applications for Scaffolding Nanomaterials

Yong Zhou①,②

Yong Zhou studied chemistry and physics at the University of Science and Technology of China (USTC), received his Master degree in 1996, and finished the PhD thesis there in 2000. After working at the Kyoto University, Japan from 2000 to 2001, he joined the group of Professor Markus Antonietti at the Max Planck Institute of Colloids and Interfaces in Germany as an Alexander von Humboldt (AvH) Fellow from 2001 to 2003. Then, he moved as a Japan Science and Technology (JST) fellow to the National Institute of Materials Science (NIMS) in 2003, and National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, in 2004. Dr. Yong Zhou worked for one year in National University of Singapore (NUS) before he settled down in Nanjing University in 2009. Until now Dr. Zhou has authored and co-authored over 60 publications including several review papers, book chapters and over 40 original articles. He is also the editorial board members of several international journals.

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Abstract

Learning from nature's amazing ability to form highly ordered structures, designed lipid and peptide molecules can organize in liquid media into open ended, hollow cylindrical structures through noncovalent self-assembly. The generated lipid nanotubes (LNTs) and peptide nanotubes (PNTs) represent a potentially powerful architecture, and are considered among the largest self-organized non-living structures yet observed. LNTs and PNTs have hydrophilically internal and external membrane surfaces, and can provide the wide scope for chemical modifications, in sharp contrast to carbon nanotubes. These unique properties make themselves as ideal candidates for a variety of applications in chemistry, biochemistry, materials science and medicine. This chapter provides recent progress in the formation of the LNTs and PNTs and their application as templates for structured nanomaterials.

1.1 Introduction

In the "bottom-up" process, simple building blocks interact with each other in a coordinated way to form large and more complex supremolecular assemblies. Molecular self-organization and self-assembly are processes by which nature builds complex, three-dimensional, multicomponent structures with well-defined functions, starting from simple building blocks such as oligonucleotides, oligosaccharides, phospholipids, proteins or peptides[1]. Learning from Nature, increasing interest has been focused on supramolecular self assembly of small organic molecules to give organized materials with macroscopically well-defined shapes and structures via molecular-recognition functions and noncovalent interactions such as electrostatic interactions, hydrogen bonds, π–π stacking, hydrophobic and van der Waals interactions since 1980s[2]. This supramolecular assembly offers numerous opportunities for chemical variation and provides an important direction for the controlled fabrication of a new class of nanoscopic materials and devices[3]. Thus, the

realization of self assembly will have far-reaching significance for not only fundamental understanding but also important applications.

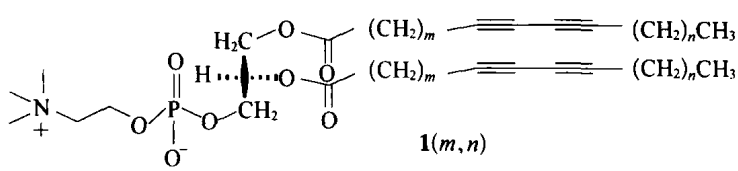
Lipid is the basic building blocks of biological membrane, and peptides are always found in proteins. In liquid media, designed lipid and peptide molecules self-assemble into open ended, hollow cylindrical structures, named lipid nanotubes (LNTs) and peptide nanotubes (PNTs), respectively[4]. LNTs and PNTs possess biocompatibility and chemical diversity with tunable surface characteristics and internal diameters, and represent a potentially powerful architecture generated through self-assembly of amphiphilic molecules. They are also much more stable and robust and can be readily synthesized on a large scale. In recent years, benefiting from the specific properties of lipid and peptide molecules like highly order architecture and precise molecular recognition, such tubular structures may offer a variety of applications in chemistry, biochemistry, materials science and medicine, biosensors, tissue engineering.

Similar to other tubular biomolecular structure such as protein microtubules[5] and tobacco mosaic virus[6], LNTs and PNTs have been becoming promising scaffolds for nanostructures[7]. On one hand, the hollow cylinder of LNTs and PNTs can provide the nanospace to confine synthesis and arrangement of nanomaterials. On the other hand, the lipid and peptide headgroups can direct the nucleation, growth and deposition of inorganic substances on the external and internal surfaces of preformed LNTs and PNTs. This chapter represents an overview of the formation of LNTs and PNTs, and their recent promising applications as templates for structured nanomaterials.

1.2 Formation of LNTs

Yagar and Schoen of the US Naval Research Laboratory first reported hollow cylindrical structures of lipid derived from 1,2-bis(tricosa-10,12-diynoyl)-*sn*-glycero-3-phospho-choline **1**(8,9) in 1984 when they studied the properties of the diacetylenic monomeric lipid[8]. They dispersed **1**(8,9) in distilled water above its chain melting transition temperature (T_m) and subsequent cooling. When aqueous dispersions were cooled below the gel-to-

liquid crystalline phase transition temperature, the 1(8, 9) lipid bilayer transited from the chain disordered L_α phase into an ordered $L_{\beta'}$ gel phase, and the tubular structure was spontaneously formed from fusion of lipid vesicles. These formed tubules were morphologically analogous to soda straws with diameters of approximately 400–1 000 nm, wall thickness of 2–10 bilayers (10–50 nm) and lengths varying from a few to several hundred micrometers. The tubule structures produced can be polymerized to render them mechanical, thermal, and chemical stability by exposure to a UV lamp or γ irradiation, or a suitable polymerization reaction. Lately, it was found that the tubules can be formed by different processes. In addition to formation in aqueous solutions, a more easy and convenient process for large amounts of the LNT was developed with ethanol/lipid/water solution[9]. The process involves dissolving the lipids in alcohol and then mixing with water above their T_m and slowly cooling the mixture. By this route longer and more robust LNTs can be produced. Aging under suitable conditions may obtain tubules in excess of 1.2 mm in length. Nevertheless, bulk water is not a prerequisite for tubule formation. The tubules may also precipitate from acetonitrile in absence of water[10]. This finding may have important technological implications in the development of these unique microstructures for promising use in organic solvents and under controlled environmental conditions. Until now 17 different diacetylenic lipids have been prepared to form the LNT[11]. Moreover, besides the family of diacetylenic lipids, several other classes of amphiphiles have also been explored to create LNTs, including peptidic-lipid[12], bolaamphiphiles[13], and glycolipid conjugates[14].



1(*m*,*n*)

Since the discovery of the LNTs, much efforts have been contributed to understanding their tubular formation mechanism. A variety of theoretical models have been proposed to explain the growth of these high-curvature structures. Among the models, the most reasonable one is based on the molecular chiral packing, which is consistent with the experiments well[15, 16]. In the most simplistic illustration in Figure 1.1, chiral self-assembly involves a

helically coiled ribbon structure as an intermediate through morphological fusion of vesicles in cooling process, which has been evidenced with experimental observation[17]. Chiral interactions cause constituent molecules to pack at a nonzero angle with respect to their nearest neighbors in the solid bilayer membrane. This situation leads to the solid bilayer ribbon to twist into an open helix, which eventually closes to yield nanotubes in the way of either widening of the tape width and maintenance of a constant helical pitch (Figure 1.1(a)) or shortening of the helical pitch of the ribbon and maintenance of a constant tape width (Figure 1.1(b)). In addition to the twisting-induced LNT, there is another route based on packing directed self-assembly[14b, 14c]. Wedge-shaped bolaamphiphilic molecules have a tendency to directly assemble into hollow cylindrical structures without forming helically twisted or coiled ribbons during the course of self-assembly.

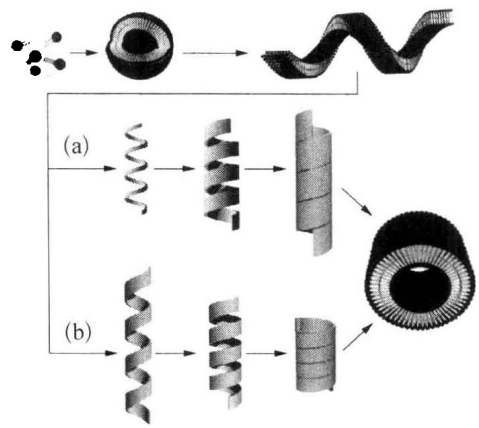


Figure 1.1 Possible formation mechanism of LNTs based on chiral molecular self-assemble.

Although the optimum mechanism behind the formation of the tubules has been identified to explain current experimental results, several fundamental questions on tubules have still risen such as: (1) what kind of materials will form these structures? (2) what is the molecular basis for the formation of the tubule structures? As a result, it is necessary to develop a rational understanding of the relation between the individual component molecule and the tubular microstructure derived from it. It has been revealed that the lipid molecular conformation, a variety of functionalities necessary for aggregation, and the location and orientation of those functionalities play crucial roles in determining the tubular self-assembling behavior[18, 19]. In general, tubular formation depends on some typical parameters such as the degree of hydration of the lipid head group, the crystallinity of the membrane and the chirality as well as presence of amide bond and hydrogen bonding[20-24]. Singh et al has synthesized a number of molecules **1**(m, n) with m varying form 4 to 15 and n varying from 6 to 17 to assess the effect of variation of these features on the self-assembly of cylindrical microstructures[25]. The most prominent results of these studies were: (1) The nondiacetylenic version of

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