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微纳米结构的导电聚合物

Conducting Polymers with Micro or Nanometer Structure

Meixiang Wan

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内 容 简 介

导电聚合物打破了聚合物为绝缘体的传统观念，因而被称为“第四代聚合物”。它既具有金属和半导体的导电特性，又保留了聚合物的轻质、柔性和可加工的特色。这种材料在光电子器件、传感技术、分子电子学和纳米器件以及驱动器件等方面具有潜在的应用前景。本书比较完整、系统地介绍了导电聚合物的缘起、掺杂与导电机制、结构与性能、技术应用前景以及研究进展，特别介绍了作者采用无模板自组装方法在微纳米结构的导电聚合物的研究及其应用方面的学术贡献。本书的内容分为5章：第1章，导论；第2章，优异的导电聚苯胺；第3章，导电聚合物的物理特性及其应用；第4章，导电聚合物的微纳米结构；第5章，无模板法自组装导电聚合物的微纳米结构。为了便于读者阅读，作者还特别给出了名词解释。

本书适合高校和科研院所的化学、化工、物理及材料专业的研究人员、教师和研究生阅读参考。

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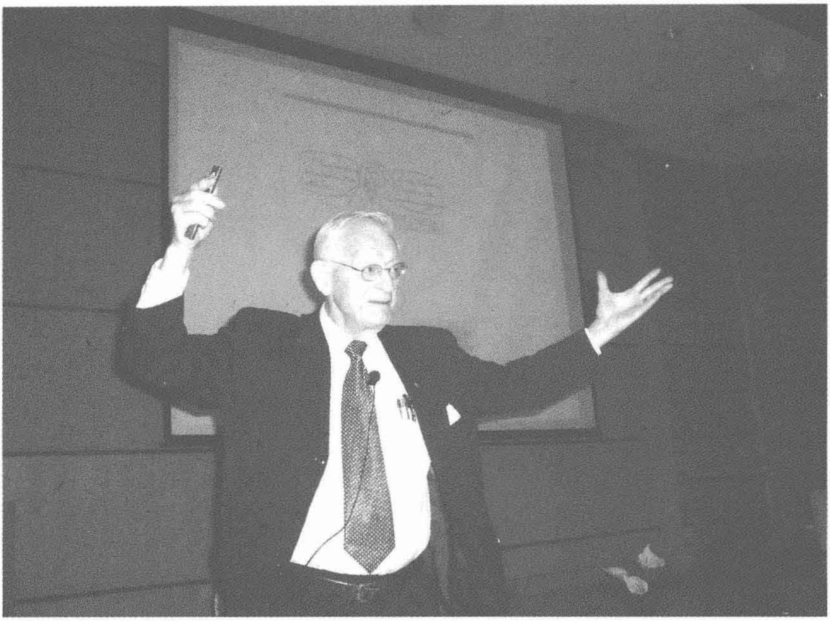
To my teacher and friend, Prof. Alan G. MacDiarmid at the University of Pennsylvania, USA, who had passed away in 2007.



Prof. MacDiarmid gave a report when he visited Institute of Chemistry, Chinese Academy of Sciences in 2004.

Author visited Professor MacDiarmid at his office, University of Pennsylvania, USA in 2004.

About Author

Meixiang Wan was born in Jiangxi Province, China, in 1940 and graduated from Department of Physics at University of Science and Technology of China in 1965. She joined the Institute of Chemistry, Chinese Academy of Sciences in 1972 in the Laboratory of Organic Solid State established by Prof. Renyuan Qian, an academy member of Chinese Academy of Sciences, to study electrical properties of organic solid states including organic photo-conductor, conductor and conducting polymers. In 1985, as a post-doctor she was fortunately recommended by Professor Qian to further pursure advanced studies on conducting polymers (e. g. polyacetylene and polyaniline) under Prof. Alan MacDiarmid', who was awarded the Nobel Prize for Chemistry in 2000, at the University of Pennsylvania, Philadelphia, USA.

Since returning to China in 1988, she has studied conducting polymers in Japan, France and the United States for a short time (3 – 6 months) as a visiting professor and often attends a variety of international conferences in the world. In 1992, she became a professor and leaded a group to study conducting polymers of polyaniline with regard to the mechanism of proton doping, electrical, optic and magnetic properties and related mechanism as well as application of electro-magnetic functionalized materials such as the microwave absorbing materials. In addition, she studied the origin of intrinsic ferromagnetic properties of organic ferromagnets. In 1988, she discovered that conductive nanotubes of polyaniline could be synthesized by *in-situ* doping polymerization in the presence of β-naphthlene surfonaic acid as a dopant, without using any membrane as a hard-template. This novel method is referred to as the template-free method due to the absence of a membrane as a template. Since discovery of the new method, her research has focused on nanostructures of conducting polymers, especially synthesized by a template-free method. So far, more than 200 papers have been published in *Advanced Materials, Chemical Materials, Micromolecules, Langmuir,* and some of them have been cited for more than 2000 times. Moreover, eight books chapters written in Chinese have been published, including "*Conducting Polymer*

Nanotubes" which was selected as a chapter in *Encyclopedia of Nanoscience and Nanotechnology* edited by H. S. Nalwa, America Scientific Publisher in 2004. In addition, ten Chinese patents were granted and several prizes, such as the Prize of the National Natural Sciences of China (second degree, 1988), the Prize of Advanced Technology of the Chinese Academy of Sciences (second degree, 1989), the Prize of Natural Sciences of the Chineses Academy of Sciences (first degree, 1995), Outstanding Younger Scientists of Chinese Academy of Sciences (1996) and Excellent Doctoral Teachers of the Chinese Academy of Sciences (2005) were awarded.

Preface

A traditional idea is that organic polymer is regarded as an excellent insulator because of its saturated macromolecule. However, a breakthrough of organic polymer imitating a metal was coming-out in the 1960s—1970s. It implied electrons in polymers need to be free to move and not bound to the atoms. The breakthrough was realized by awarders of Nobel Chemistry Prizes in 2000, who were Alan J. Heeger at the University of California at Santa Barbara, USA, Alan G. MacDiarmid at the University of Pennsylvania, Philadelphia, USA, and Hideki Shirakawa at the University of Tsukuba, Japan. In 1977, actually, they accidentally discovered that room-temperature conductivity of conjugated polyacetylene doped with iodine was as high as 10^3 S/cm, which was enhanced by 10^{10} times compared with original insulating polyacetylene. The change of the electrical properties from insulator to conductor was subsequently ascribed to "doping", but completely different from the doping concept as applied in inorganic semiconductors. The unexpected discovery not only shattered a traditional idea that organic polymers are insulators, but also established a new filed of conducting polymers or "synthetic metals".

Since discovery of the first conducting polymer (i.e. polyacetylene), conducting polymers have been received considerable attention because of their unique properties such as highly-conjugated chain structure, covering whole insulator-semiconductor-metal region of electrical properties, a reversible doping/de-doping process, an unusual conducting mechanism and the control of physical properties by the doping/de-doping process. The unique properties not only lead to promising applications in technology, but also hold an important position in material sciences. Up to date, the potential applications of conducting polymers include electronic devices (e.g. Schottky rectifier, field-effect transistor, light emitting diode and solar cell), electromagnetic interference shielding and microwave absorbing materials, rechargeable batteries and supercapacitors, electrochromic devices, sensors (e.g. gas, chemical and biochemical sensors) and artificial muscles. As a result, research on conducting polymers has spread rapidly from the United States.

Moreover, the significant progress on conducting polymer synthesis, new materials, conducting and transport mechanisms, processability, structure-property relationship and related mechanisms as well as applications have been achieved. After 23 years, conducting polymers, awarded the 2000 Nobel Prize in Chemistry, have affirmed contributions of the above-mentioned three scientists for the discovery and development of conductive polymers, and also for further promoting the development of conducting polymers.

Proferssor Renyuan Qian as an academy member of the Chinese Academy of Sciences, for the first time, established a laboratory of entilted organic solid state at the Institue of Chemistry, Chinese Academy of Sciences in the early 1980s. The research has covered synthetic method, structureal characterization, and the optical, electrical and magnetic properties and related mechanisms of organic solid states photoconductors, conductors, superconductors and ferromagnets as well as conducting polymers.

I was fortunate to enter the laboratory recommended by Professor Qian, to study electrical properties of organic photoconductors, conductors and conducting polymers. In 1985, I was again recommended by Professor Qian to pursure advanced studing on conducting polymers under Professor MacDiarmid as a post-doctor. In USA, I studied photo-electro-chemistry of polyaniline, which was discovered by Professor MacDiarmid in 1985 for the first time. Compared with other conducting polymers, polyaniline is advantageous of simple and low cost synthesis, high conductivity and stability, special proton doping mechanism and controlling physical properties by both oxidation and protonation state, resulting in a special position in the field of conducting polymers. These novel physical properties and promissing potential applications in technology therefore promissed me to study continuously polyaniline when I came back from USA to China in 1988.

Since discovery of carbon nanotube in 1991, nanoscience and nanotechnology have become some of the fastest growing and most dynamic areas of research in the 20^{th} centrury. Scientifically, "nano" is a scale unite that means 1 nanomerter, one billionth of a meter (10^{-9} m). Generally speaking, therefore, the nanomaterials are defined structural features in the range of 1 – 100 nm. Based on the definition, it is understood that nanotechnology deals with atomic and molecular scale functional structures. With nano-scaled features but large surface area, nanomaterials offer unique and entirely different properties compared with their bulk materials. Thereby, the unique properties of nanomaterials result in nanomateials and nanotechnology rapidly spreading to academic institutes and industries around the world.

In the 1990s, I accidentally found that nanotubes of polyaniline could be prepared by a conventional *in-situ* doping polymerization in the presence of nanphthalene surfonic acid as the dopant without using any membrane as the template. The created method was latterly called as template-free method because of omitting membrane as a template. Especially, further studies demonstrated that essency of the method belongs to self-assembly process because the micelles composed of dopnat, dopant/monomer salt or supermolecules even monomer itself are served as the soft-templates in the formation of the template-free synthesized nanostructures of conducting polymers. Compared with the template-synthesis method, which was commonly used, the efficient and controlled approach to prepare conducting polymer nanostructures is simple and inexpensive because of the lack of template and the post-treatment of template removal. However, many questions dealing with this method were completely un-understood at that time. For instance, how about the universality of the method to nanostructures of conducting polymers? What is formation mechanism of the self-assembled nanostructures by the method? How about controllability of the morphology and size for the template-free synthesized nanostructures? Do the electrical properties of the template-free synthesized nanostructures differ from the bulk materials? Is it possible to fabricate multi-functionalized nanostructures of conducting polymers based on template-free method? Can we identify applications for the template-free synthesized nanostructures? All above-mentioned issues promised me to systematically and significantly study nanostructures of conducting polymers by a template-free method.

In fact, the significant progress on conducting polymer nanostructures by the method has been achieved. In 2006, Tsingua University Press in Beijing and Springer-Verlag GmbH in Berlin invited me to write a book about conducting polymers and related nanostructures. Although a lot of good books and excellent reviews on conducting polymers and corresponding nanostructures have been widely published in the world, I was eager to share my knowledge and experience on studying conducting polymers and their nanostructures with other scientists, teachers and students who are interested in conducting polymers. I therefore was pleased to accept the invitation to write up this book.

The book consists of five chapters. The first chapter briefly introduces basic knowledge of conducting polymers, such as doping item, conducting mechanism, structural characteristics and physical properties of conducting polymers. The second chapter further considers structural characteristic, doping mechanism, processability and structure-property relationship of conducting polymers using polyaniline as an example. The third chapter mainly reviews physical properties and corresponding potential application of conducting polymers in technology. The fourth chapter summarizes progress and developing directions in conducting polymer nanostructures, dealing with synthesis method, unique properties and fabricating technology of nano-arrays, patents, and potential application in technology. The fifth chapter mainly reviews results on template-free synthesized conducting polymer micro/nanostructures focusing on the universality, controllability and formation mechanism of the method, multifunctional nanostructure based on template-free method associated with other approaches, electrical and transport properties of the self-assembled nanostructures, especially electrical and transport properties of a single nano-tube or hollow sphere, as measured by a four-probe method, and applications as microwave absorbing materials and gas sensors guided by reversible wettability. I hope this book is able to provide some basic and essential reference information for those studying conducting polymers and their nanostructures.

I am very grateful to Professor Alan G. MacDiarmid and Renyuan Qian for bringing me to enter the field of conducting polymers. I am benefited lifelong for their keep improving and conscientiously in sciences. Although both Professor Alan G. MacDiarmid and Renyuan Qian as my kindness teachers have passed away, their early influence and mentoring are deeply appreciated. I sincerely thank all my coworkers and students for their excellent contributions to this book. I especially express my sincere gratitude to my father and mother for their rear kindness, and to my husband, son, and daughter for their love as well as to relatives and friends for their help and friendship.

Contents

Chapter 1 Introduction of Conducting Polymers

According to electrical properties, materials can be divided into four-types: insulator, semiconductor, conductor and superconductor. In general, a material with a conductivity less than 10^{-7} S/cm is regarded as an insulator. A material with conductivity larger than 10^{3} S/cm is called as a metal whereas the conductivity of a semiconductor is in a range of $10^{-4} - 10$ S/cm depending upon doping degree. Organic polymers usually are described by σ (sigma) bonds and π bonds. The σ bonds are fixed and immobile due to forming the covalent bonds between the carbon atoms. On the other hand, the π-electrons in a conjugated polymers are relatively localised, unlike the σ electrons. Plastics are typical organic polymers with saturated macromolecules and are generally used as excellent electrical insulators. Since discovery of conductive polyacelene (PA) doped with iodine [1], a new field of conducting polymers, which is also called as "synthetic metals", has been established and earned the Nobel Prize in Chemistry in 2000 [2]. Nowadays, conducting polymers as functionalized materials hold a special and an important position in the field of material sciences. In this Chapter, discovery, doping concept, structural characteristics, charge transport and conducting mechanism for the conducting polymers will be brief discussed.

1.1 Discovery of Conducting Polymers

In the 1960s—1970s, a breakthrough, polymer becoming electrically conductive, was coming-out. The breakthrough implied that a polymer has to imitate a metal, which means that electrons in polymers need to be free to move and not bound to the atoms. In principle, an oxidation or reduction process is often accommpanied with adding or withdrawing of electrons, suggesting an electron can be removed from a material through oxidation or introduced into a material through reduction. Above idea implies that a polymer might be electrically conductive by withdrawing electron through oxidation (i.e. a "hole") or by adding electron through reduction, which process was latterly described by an item of "doping". The breakthrough was realized by three awarders of Chemistry Nobel Prize in 2000, who were Alan J. Heeger at the University of California at Santa Barbara, USA, Alan G. MacDiarmid at the University of Pennsylvania, Philadelphia, USA, and Hideki Shirakawa at the University of Tsukuba, Japan [2]. In 1977, they accidentally discovered that insulating π-conjugated PA could become conductor with a conductivity of 10^3 S/cm by iodine doping [1]. The unexpected discovery not only broken a traditional concept, which organic polymers were only regarded as the insulators, but also establishing a new filed of conducting polymers, which also called as "Synthetic Metals". According to a report of the Royal Swedish Academy of Sciences in 2000 [2], there was an interesting story about discovery of the conducting polymers. Since accidental discovery in science often happens, author would like to briefly introduce the story to share with readers. Based on above idea of polymer imitating a metal, scientists thought that PA could be regarded as an excellent candidate of polymers to be imitating a metal, because it has alternating double and single bonds, as called conjugated double bonds. From Fig. 1.1, one can see, PA is a flat molecule with an angle of 120° between the bonds and hence exists in two different forms, the isomers *cis*-polyacetylene and *trans*-polyacetylene [2].

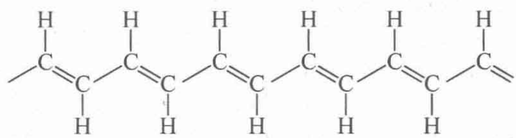


Figure 1.1 Molecular structure of polyacetylene [1, 2]

Thereby, synthesis of PA received great of attention at that time. At the beginning of the 1970s, Hedeki Shirakawa at Tokyo Institute of Technology, Japan, was studying the polymerization of acetylene into plastics by using catalyst created by Ziegler-Natta, who was awarded the 1963 Nobel Prize of Chemistry for a technique of polymerizing ethylene or propylene into plastics. Usually, only the form of black powder could be synthesized by using the conventional polymerization method. A visiting scientist in Shirakawa's group tried to synthesize PA in the usual way. However, a beautifully lustrous silver colored film, rather than the black powder synthesized by the conventional method, was obtained. The unexpected results promissed Shirakawa to check the polymerization conditions again and again, and Shirakawa finally found that the catalyst concentration used was enhanced by 10^3 times! Shirakawa was stimulated by the accidental discovery and further found the molecular structure of the resulting PA was affected by reaction temerature, for instance, the silvery film was *trans*-polyacetylene whereas copper-colored film was almost pure *cis*-polyacetylene.

In another part of the world, chemister Alan G. MacDiarmid and physicist Alan J. Heeger at University of Pennsylvania, Philadephia, USA were studing the first metal-like inorganic polymer sulphur nitride ($(SN)_x$), which is the first example of a covalent polymer without metal atoms [3]. In 1975, Prof. MacDiarmid visited Tokyo Institute of Technology and gave a talk on $(SN)_x$. After his lecture, MacDiarmid met Shirakawa at a coffee break and showed a sample of the golden $(SN)_x$ to Shirakawa. Consequently, Shirakawa also showed MacDiarmid a sample of the silvery $(CH)_x$. The beautiful silvery film caught the eyes of MacDiarmid and he immediately invited Shirakawa to the University of Pennsylvania in Philadelphia to further study PA. Since MacDiarmid and Heeger had found previously that the conductivity of $(SN)_x$ could be increased by 10 times after adding bromine to the golden $(SN)_x$ material, which is called as "doping" item in inorganic semiconductor. Therefore, they decided to add some bromine to the silvery $(CH)_x$ films to see what was happen. Miracle took place on November 23, 1976! At that day, Shirakawa worked with Dr. C.K. Chiang, a postdoctoral fellow under Professor Heeger, for measuring the electrical conductivity of PA by a four-probe method. Surprise to them, the conductivity of PA was ten million times higher than before adding bromine. This day was marked as the first time observed the "doping" effect in conducting polymers. In the summer of 1977, Heeger, MacDiarmid, and Shirakawa co-published their discovery in the article entitled "Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene $(CH)_n$" in *The Journal of Chemical Society, Chemical Communications* [1].

After discovery of the conductive PA, fundamental researches dealing with synthesis of new materials, structural characterization, solubility and processability, structure-properties relationship and conducting mechanism of conducting polymers as well as their applications in technology have been widely studied and significant progress have been achieved. After 23 years, The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Chemistry for 2000 jointly to Alan J. Heeger at University of California at Santa Barbara, USA, Alan G. MacDiarmid at University of Pennsylvania, Philadelphia, USA, and Hideki Shirakawa at University of Tsukuba, Japan "for the discovery and development of conductive polymers" [2]. Photograph of the three scientists are shown as Fig. 1.2. Nowadays, the field of conducting polymers had been well established

Figure 1.2 Photograph of three awardees of the Nobel Chemistry Prize in 2000
Alan G. MacDiarmid (left) Prof. at the Univ. of Pennsylvania, USA
Hideki Shirakawa (middle) Prof. Emeritus, Univ. of Tsukuba, Japan
Alan J. Heeger (right) Prof. at the Univ. of California at Santa Barbara, USA