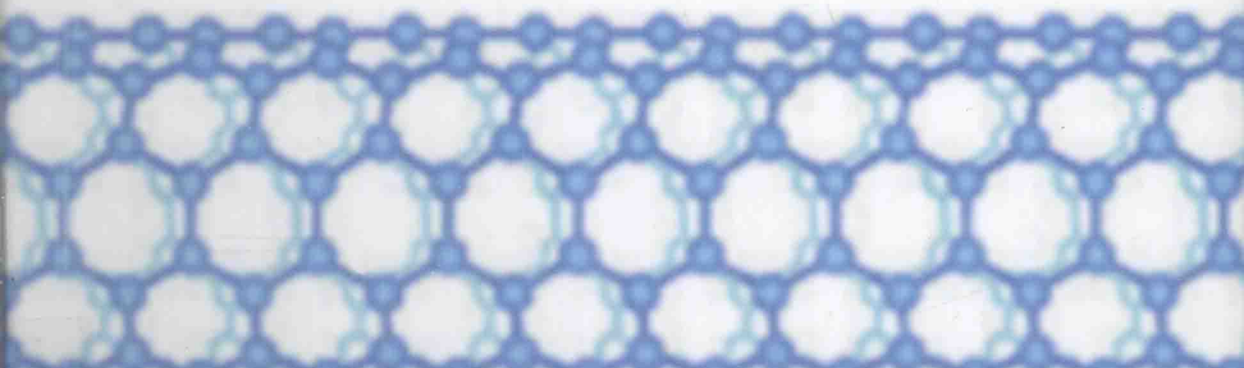
Carbon Nanotubes and Graphene

碳纳米管和石墨烯

Zhao Tingkai Li Tiehu Liu Yongning



Science Press
Beijing

Carbon Nanotubes and Graphene

(碳纳米管和石墨烯)

Zhao Tingkai Li Tiehu Liu Yongning

Science Press
Beijing

Responsible Editors: Li Ping, Yang Xiangping, Ji Siwen

Published by Science Press
16 Donghuangchenggen North Srteet
Beijing 100717, P. R. China

Printed in Beijing

ISBN 978-7-03-040052-9 (Beijing)

Foreword

The nanoscience and technology has had an extraordinary season of development and excitement in the last few decades. Furthermore, advanced carbon nanomaterial is one of the most active and hot research fields in the world. The potential applications of advanced carbon nanomaterials now enjoy worldwide attention. Especially, carbon nanotubes and graphene appear to take a lead in their applications. Carbon nanotubes and graphene are nanostructured carbon materials having large aspect ratios, extremely high Young's modulus and mechanical strength, as well as superior electrical and thermal conductivities. Incorporation of a small amount of carbon nanotubes or graphene into metals and ceramics leads to the formation of high performance and functional nanocomposites with enhanced mechanical and physical properties.

This book is was constructed in the contents based on the summarizing and expanding of the authors' research achievements and the published literatures. The contents include synthesis, characterization, property and application of carbon nanotubes and graphene, especially amorphous carbon nanotubes. Electrochemical devices, solar cells, lithium ion batteries and electromagnetic wave absorbing materials using carbon nanotubes and graphene are also becoming very promising areas, especially in military field. Carbon is biologically compatible, so carbon nanotubes and graphene composites are attracting attention for their application in biotechnological system such as drug delivery and so on. This book also serves as a valuable and useful reference book for chemists, materials scientists, physicists and other researchers working in this field. I'm looking forward to that this book will give a valuable reference for these researchers in carbon nanomaterials field.

Bingbo Wei

Academician of Chinese Academy of Sciences
Professor, Northwestern Polytechnical University

Preface

Nanotechnology is almost a household word nowadays, or at least some words with "nano" in it, such as nano-cloth or nano-machine and so on. This field now enjoys worldwide attention. Especially, carbon nanomaterials appear to take a lead in their applications.

The important areas are synthesis, characterization, property and application of carbon nanomaterials, especiallies carbon nanotubes and graphene. With a better understanding of the processing-structure-performance relationship, carbon nanomaterials with predicted and tailored physical/mechanical properties as well as good biocompatibility can be designed and fabricated. Electrochemical devices, solar cells, lithium ion batteries and electromagnetic wave absorbing/shielding materials using carbon nanotubes and graphene are also becoming very promising areas, and very soon they will become reality in their applications. Carbon nanotubes and graphene are attracting attention for their application in biotechnological system such as drug delivery and so on. Therefore, there is a need to write a book for serving the basic science community, especially material scientist and chemists.

This book consists of five chapters selected from our research achievements and a proportion from published literatures. The coverage of this book is as follows: first chapter (written by Prof. Li and Prof. Liu), an introduction of carbon nanomaterilas and a brief historical description are given; the other four chapters (written by Prof. Zhao) deal more with the synthesis and properties, such as physical and chemical properties, and several applications of carbon nanotubes and graphene.

This book was written to serve as one of the textbooks for senior undergraduate, graduate and oversea students, also as a resource and reference book for material scientists, chemists and other researchers working in this field. I would like to thank the support of Northwestern Polytechnical University Publication Fund and Science Press, and the help of my students (Dr. Zhao and Dr. Liu) and colleague

(Prof. Liu at Northwestern University in USA), as well as my family for their patience and understanding.

Zhao Tingkai
Northwestern Polytechnical University
in Xi'an

Acknowledgements

We're sincerely thankful for all the authors and contributors for their high-quality and timely contributions such as these cited papers, books and patents, who are world renowned experts in this burgeoning field of nanotechnology. Their enthusiasm and hard work are very much appreciated. We would also like to thank the financial support of Northwestern Polytechnical University Publication Fund, and Science Press for their encouragement and patience. We also acknowledge the help of our students (Dr. Zhao Xing, Dr. Liu Lehao, etc.) and colleague (Prof. Liu Zhifu at Northwestern University in USA).

Contents

Chapter 1
Carbon nanomaterials

1.1 Fundamental concepts of nanomaterials and carbon

Nano is a prefix to a word. It is similar with "kilo" or "macro" etc. Generally, nano as a prefix is usually used in the unit of length or other unit, such as nanometer (metre), nanoampere and so on.

1.1.1 Nanometer

Nanometer (abbr. nm) is a unit of length.

One nanometer (1nm) is one billionth (10^{-9}) of a meter. By comparison, typical carbon-carbon bond lengths, or the spacing between these atoms in a molecule, are in the range of 0.12～0.15nm, and a DNA double-helix has a diameter of around 2nm. Besides, the smallest cellular life-forms, the bacteria of the genus mycoplasma, are around 200nm in length[1]. The human hair is about 80 000nm in width[2].

As mentioned above, materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper)[3], inert materials attain catalytic properties (platinum)[4], stable materials turn combustible (aluminum)[5], solids turn into liquids at room temperature (gold)[6], insulators become conductors (silicon)[7]. Materials such as gold, which is chemically inert at normal scales, can serve as a potential chemical catalyst at nanoscales[8]. Much of the fascination with nanotechnology stems from the unique quantum and surface phenomena of matters exhibit at the nanoscale. For example, if you take aluminum and cut it in half, it is still aluminum. But if you keep cutting aluminum in half until it has dimensions on the nano scale, it becomes highly reactive. This is because the molecular structure is changed.

Nanosized powder particles (a few nanometres in diameter, also called nanoparticles) are potentially important in ceramics, powder metallurgy, uniform nanoporosity and similar applications. The strong tendency of small particles to form clumps ("agglomerates") is a serious technological problem that impedes such applications. However, a number of dispersants such as ammonium citrate (aqueous) and imidazoline or oleyl alcohol (nonaqueous) are promising solutions as possible additives for deagglomeration.

Nanomaterial is a field that takes a material science-based approach to nanotechnology. It studies materials with morphological features on the nanoscale, and especially those with special properties stemming from their nanoscale dimensions. Nanoscale is usually defined as smaller size than one tenth of a micrometer (μm) in at least one dimension, though this term is sometimes also used for materials smaller than one micrometer.

Much of nanoscience and many nanotechnologies are concerned with producing new or enhanced materials. Nanomaterials can be constructed by "top-down" technique, producing very small structures from larger pieces of material, for example by etching to create circuits on the surface of a silicon microchip. They may also be constructed by "bottom-up" technique, atom by atom or molecule by molecule. One way of doing this is self-assembly, by which the atoms or molecules arrange themselves into a structure due to their natural properties. Crystals grown for the semiconductor industry provide an example of self-assembly, as chemical synthesis of large molecules. The second way is to use tools to manipulate atom or molecule individually. Although this "positional assembly" offers greater control over construction, it is currently very laborious and not suitable for industrial applications[9].

It has been 29 years since the scanning tunneling microscope (STM) was invented, followed six years later by the atomic force microscope (AFM), and that's when nanoscience and nanotechnology really started to take off. Various forms of scanning probe microscopes (SPM) based on these discoveries are essential for many areas of today's research. Scanning probe techniques have become the workhorse of nanoscience and nanotechnology research.

Current applications of nanoscale materials include very thin coatings used in electronics and active surfaces (such as self-cleaning windows). In most applications the nanoscale components will be fixed or embedded. But in some applications, such as those used in cosmetics and in some pilot environmental remediation applications, free-nanoparticles are used. The ability to machine materials to very high precision and accuracy (less than 100nm) is leading to considerable benefits in a wide range of industrial sectors, such as in the production of components for the information and communication technology, automotive and aerospace industries.

1.1.2 Definition of nanomaterials

Although a broad definition, we categorize nanomaterials as those which have at least one dimension less than 100nm.

(1) Materials that are at the nanoscale in three dimensions (3-D) are particles, such as precipitates, colloids and quantum dots (tiny particles of semiconductor materials).

(2) Materials that are at the nanoscale in two dimensions (2-D) (and extended in one dimension) include nanowires and nanotubes.

(3) Materials that have one dimension (1-D) at the nanoscale (and are extended in the other two dimensions) are layers, such as a thin films or surface coatings. Some of the features on computer chips come in this category.

(4) Nanocrystalline materials, made up of nanometre-sized grains (0-D), also fall into this category. Some of these materials have been available for some time, others are genuinely new.

Two main factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area and quantum effects. These factors can change or enhance the properties of materials such as reactivity, strength and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface site compared with those inside. For example, a particle size of 30nm has 5% of its atoms on its surface, of 10nm has 20% of its atoms and of 3nm 50% of its atoms. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. Since growth and catalytic chemical reactions occur at these surfaces, a given mass of material in nano-particulate form will be much more reactive than the same mass of material made up of larger particles.

To understand the effect of particle size on the surface area, consider the U. S. silver dollar. The silver dollar contains 26.96g of coin silver, has a diameter of about 40mm, and has a total surface area of approximately 27.70cm^2.

If the same amount of coin silver were divided into tiny particles—say 1nm in diameter—the total surface area of those particles would be 11 400m^2. When the amount of coin silver contained in a silver dollar is rendered into 1nm particles, the surface area of those particles is 4.115 million times greater than the surface area of the silver dollar[10]!

1.1.3 The history of carbon

Carbon (pronounced /karbən/) is the chemical element with symbol C and atomic number 6. As a member of group Ⅳ on the element periodic table, it is nonmetallic and tetravalent—making four electrons available to form covalent chemical bonds. There are three naturally occurring isotopes, with ^{12}C and ^{13}C being stable, while ^{14}C is radioactive, decaying with a half-life of about 5730 years[11]. Carbon is one of the few elements known since antiquity. The name "carbon" comes from Latin language "carbo", coal and in some Romance and Slavic languages, the word "carbon" can refer both to the element and to coal.

Carbon C is one of the abundant elements on the earth. Almost all organics are composed of carbon networks, and carbon materials are very familiar in our daily lives, for example, ink for newspapers, "lead" for pencils, active carbon in refrigerators, and so on. Carbon materials, which consist mainly of carbon atoms, have been used since the prehistoric era as charcoal[12].

Carbon is one of the least abundant elements in the earth's crust, but the fourth most abundant element in the universe by mass after hydrogen, helium and oxygen. It is present in all known lifeforms and in the human body carbon is the second most abundant element by mass (about 18.5%) after oxygen. This abundance, together with the unique diversity of organic compounds and their unusual polymer-forming ability at the temperatures commonly encountered on the Earth, make this element the chemical basis of all known life (Fig. 1-1).

Carbon was discovered in prehistory and was known in the forms of soot and charcoal to the earliest human civilizations. Diamonds were known probably as early as 2500 BC in China, while carbon in the form of charcoal was made around Roman times by the same chemical process as it is today, by heating wood in a pyramid covered with clay to exclude air[13,14].

There are several allotropes of carbon of which the best known are graphite, diamond and amorphous carbon[15]. The physical properties of carbon vary widely with the allotropic forms. For example, diamond is highly transparent, while

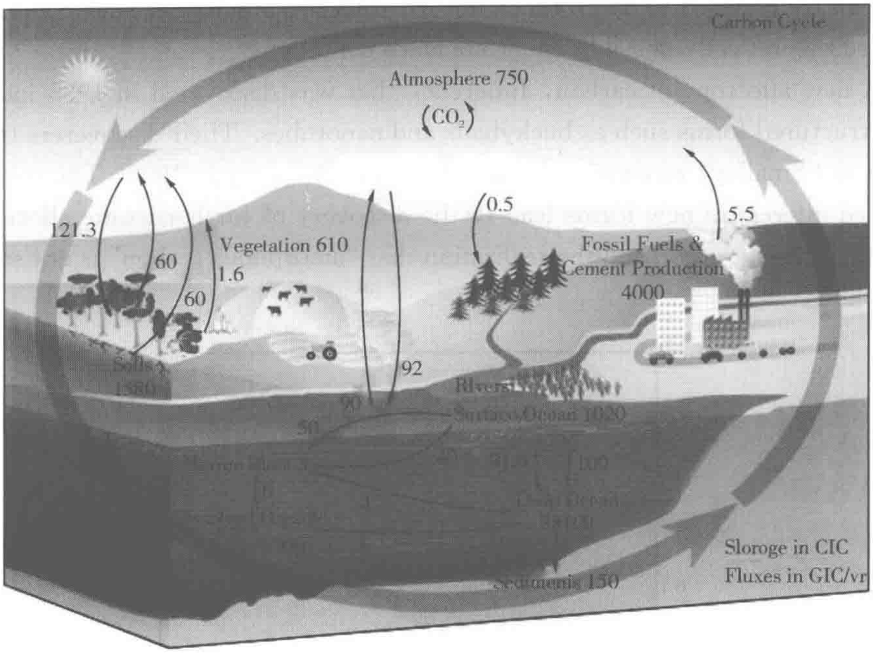


Fig. 1-1 Diagram of the carbon cycle

The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons ("GtC" stands for gigatons of carbon. figures are circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year. The sediments, as defined in this diagram, do not include the ~70 million GtC of carbonate rock and kerogen (image from NASA)

graphite is opaque and black. Diamond is among the hardest materials known, while graphite is soft enough to form a streak on paper (hence its name, from the Greek word "to write"). Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond has the highest thermal conductivity of all known materials. All the allotropic forms are solids under normal conditions but graphite is the most thermodynamically stable[16] (Table 1-1).

All forms of carbon are highly stable, requiring high temperature to react even with oxygen (Fig. 1-2). The most common oxidation state of carbon in inorganic compounds is +4, while +2 is found in carbon monoxide and other transition metal carbonyl complexes. The largest sources of inorganic carbon are limestones, dolomites and carbon dioxide, but significant quantities occur in organic deposits of coal, peat, oil and methane clathrates. Carbon forms more compounds than any other element, with almost ten million pure organic compounds described to date, which in turn are a tiny fraction of such compounds that are theoretically possible under standard conditions[17].

A new allotrope of carbon, fullerene, that was discovered in 1985 includes nanostructured forms such as buckyballs and nanotubes. Their discoverers (Curl, Kroto and Smalley) received the Nobel Prize in Chemistry in 1996. The resulting renewed interest in new forms lead to the discovery of further exotic allotropes, including glassy carbon and the realization that "amorphous carbon" is not strictly amorphous.

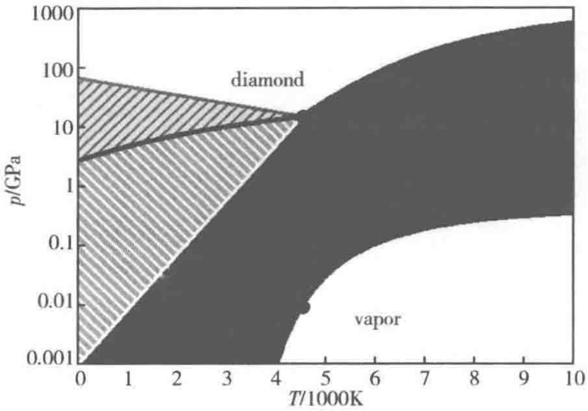


Fig. 1-2 Theoretically predicted phase diagram of carbon
(Image from English Wikipedia)

As to 2009, graphene appears to be the strongest material ever tested[18]. However, the process of separating it from graphite will require some technological development before it is economical enough to be used in industrial processes.

Table 1-1 The system of carbon allotropes spans a range of extremes

Synthetic nanocrystalline diamond is the hardest materials known	Graphite is one of the softest materials known
Diamond is the ultimate abrasive	Graphite is a very good lubricant
Diamond is an excellent electrical insulator	Graphite is a conductor of electricity
Diamond is the best known naturally occurring thermal conductor	Some forms of graphite are used for thermal insulation (i. e. firebreaks and heat shields)
Diamond is highly transparent	Graphite is opaque
Diamond crystallizes in the cubic system	Graphite crystallizes in the hexagonal system
Amorphous carbon is completely isotropic	Carbon nanotubes are among the most anisotropic materials ever produced