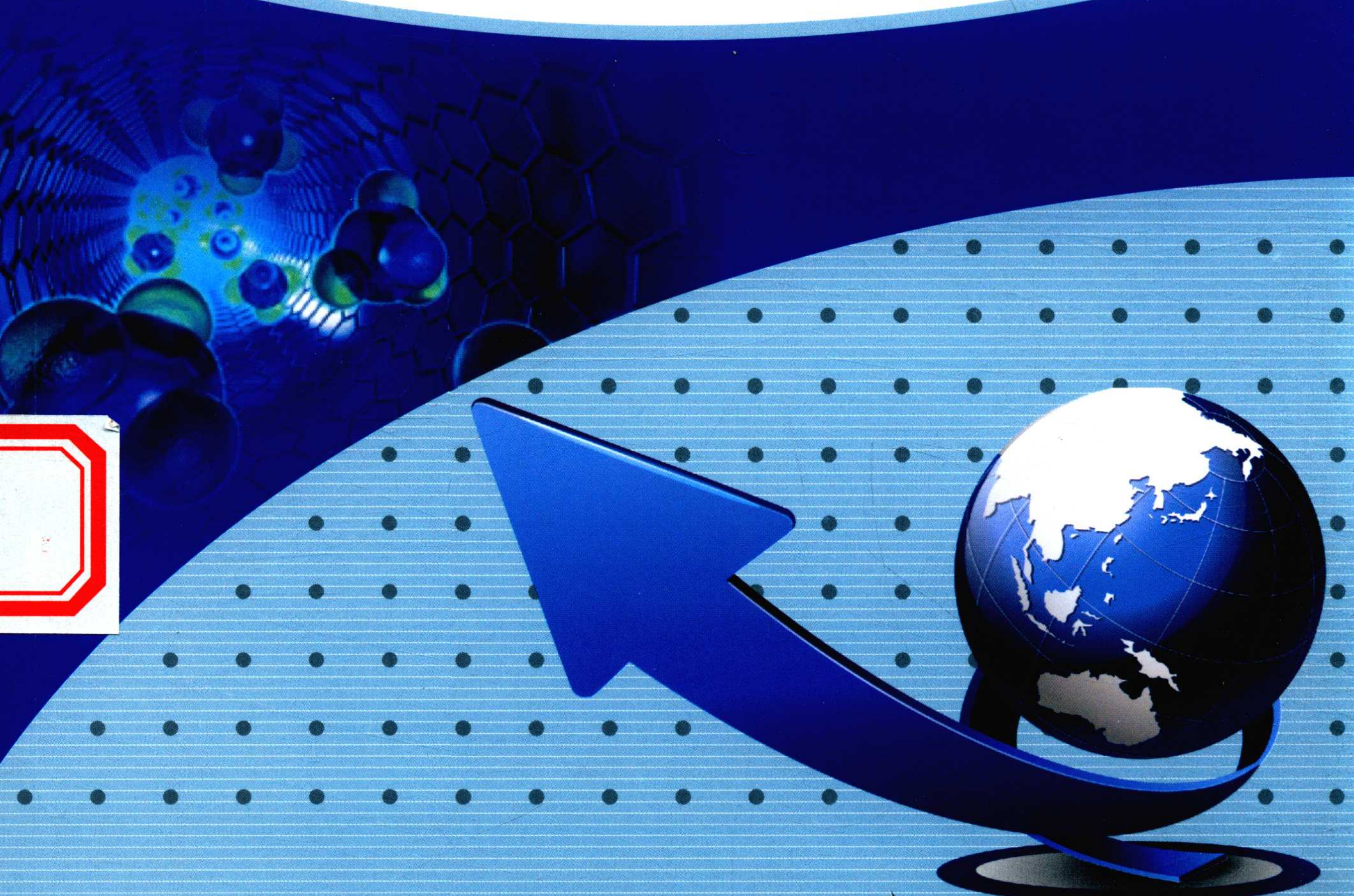
高等学校“十三五”规划教材

新型碳纳米材料

Advanced Carbon Nanomaterials

赵廷凯◎主编



西北工業大學出版社

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Edited by Zhao Tingkai
（赵廷凯）

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西 安

【Introduction of Content】 Advanced carbon nanomaterials, especially fullerene, carbon nanotubes and graphene are the hottest research topics in recent years.The investigations of fullerene, carbon nanotubes and graphene drive a full develop in the fields of new process, new method and new technology etc. and affect science technology and social development. This textbook consists of six chapters selected from the published literatures and partially from our research achievements. The coverage of this book is as follows: first two chapters are the introduction of nanotechnology and nanomaterials, and carbon and carbon nanomaterilas. Then the next four chapters deal more with the historical development, synthesis, properties(such as physical and chemical properties) and finally several applications of fullerene, carbon nanotubes and graphene.

This textbook was written to serve as one of the senior undergraduate, graduate or overseas student courses in the fields of new materials, new energy and nanotechnology, and second as a resource and reference book for material scientist and chemists and other researchers working in this field.

图书在版编目(CIP)数据

新型碳纳米材料＝Advanced Carbon Nanomaterials:英文/赵廷凯主编．—西安:西北工业大学出版社,2017.3
ISBN 978－7－5612－5280－2

Ⅰ.①新… Ⅱ.①赵… Ⅲ.①碳—纳米材料—研究—英文 Ⅳ.①TB383

中国版本图书馆 CIP 数据核字(2017)第 063313 号

策划编辑: 杨 军
责任编辑: 胡莉巾

出版发行: 西北工业大学出版社
通信地址: 西安市友谊西路 127 号　　邮编:710072
电　　话: (029)88493844　88491757
网　　址: www.nwpup.com
印 刷 者: 陕西宝石兰印务有限责任公司
开　　本: 787 mm×1 092 mm　　1/16
印　　张: 8.875
字　　数: 212 千字
版　　次: 2017 年 3 月第 1 版　　2017 年 3 月第 1 次印刷
定　　价: 29.00 元

PREFACE

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

This field owes its parentage to investigations of reactive species (free atoms, clusters, reactive particles) throughout the 1970s and 1980s, coupled with new techniques and instruments (focus ion beams, innovations in mass spectrometry, vacuum technology, microscopes, and more). Excitement is high and spread throughout different fields, including chemistry, physics, material science, engineering and biology. This is warranted because nanoscale materials represent a new realm of matter, and the possibilities for interesting basic science as well as useful technologies for society are widespread and real.

In spite of all this interest, there is a need for textbooks that serve the basic science community, especially material scientists and chemists.

This textbook "Advanced Carbon Nanomaterials" is written to serve both as one of the textbooks for senior undergraduate, graduate or overseas student courses on carbon-based nanomaterials, and as a resource and reference for material scientists and chemists and other researchers working in this field. Therefore, the readers will find that the chapters are written as a teacher might teach the subject, and not simply as a reference work. For this reason, I hope that this textbook will be adopted for teaching numerous advanced courses in nanotechnology, materials chemistry, and related subjects.

The coverage of this textbook is as follows: first, a detailed introduction of nanotechnology and a brief historical account are given. The next chapters deal more with the synthesis, structure and properties of fullerenes, carbon nanotubes and graphene, such as chemical properties, physical properties, and finally a short chapter on applications of carbon nanomaterials.

The author gratefully acknowledge the contributing authors of these literatures, who are world renowned experts in this burgeoning field of nanotechnology. Their enthusiasm and hard work are very much appreciated. The author also acknowledge the help of my students: Dr. Zhao Xing, Dr. Liu Lehao, Mr. Ji Xianglin et al, as well as my families (especially my wife Liang Jing and my daughter Zhao Xin) for their patience and understanding.

Zhao Tingkai
NPU, Xi'an
2016.12

CONTENTS

Chapter 1 Introduction

1.1 Fundamental concept of nano

Nano is a prefix to a word. It is similar with "kilo" or "macro" etc. Generally, nano as a prefix is used in the unit of length, such as nano-meter (metre). The ten SI prefixes are shown in the chart below (see Table 1 - 1).

Table 1 - 1 List of SI prefixes

10^n	Prefix	Symbol	Since	Short scale	Long scale	Decimal
10^{12}	tera	T	1960	Trillion	Billion	1,000,000,000,000
10^9	giga	G	1960	Billion	Milliard	1,000,000,000
10^6	mega	M	1960	Million		1,000,000
10^3	kilo	k	1795	Thousand		1,000
10^1	deca	da	1795	Ten		10
10^0	(none)	(none)	NA	One		1
10^{-3}	milli	m	1795	Thousandth		0.001
10^{-6}	micro	μ	1960	Millionth		0.000,001
10^{-9}	nano	n	1960	Billionth	Milliardth	0.000,000,001
10^{-12}	pico	p	1960	Trillionth	Billionth	0.000,000,000,001

1.2 Fundamental concept of nanometer

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

From Table 1 - 1, one nanometer (nm) is one billionth, or 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 0.12 - 0.15 nm, and a DNA double-helix has a diameter around 2 nm. On the other hand, the smallest cellular life-forms, the bacteria of the genus mycoplasma, are around 200 nm in length. They make a comparison with a human hair, which is about 80,000 nm wide (see Fig.1 - 1).

To put that scale in another context, the comparative size of a nanometer to a meter is the same as that of a marble to the size of the earth. Or another way of putting it: a nanometer is the amount a man's beard grows in the time it takes him to raise the razor to his face. (see Fig.1 - 2 and Fig.1 - 3)

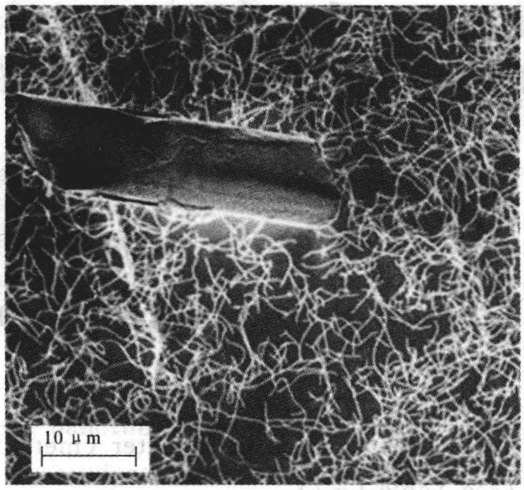


Fig. 1 - 1 Human hair fragment and a network of single-walled carbon nanotubes

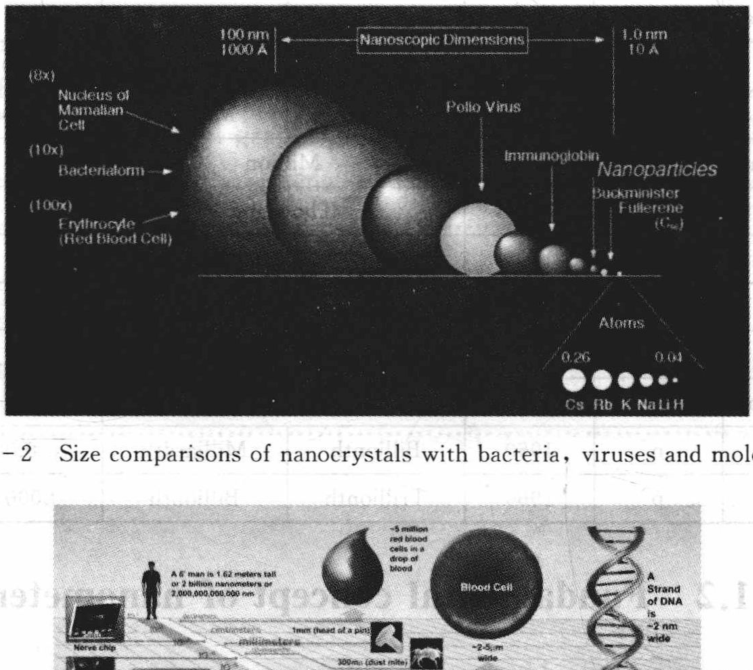


Fig.1 - 2 Size comparisons of nanocrystals with bacteria, viruses and molecules

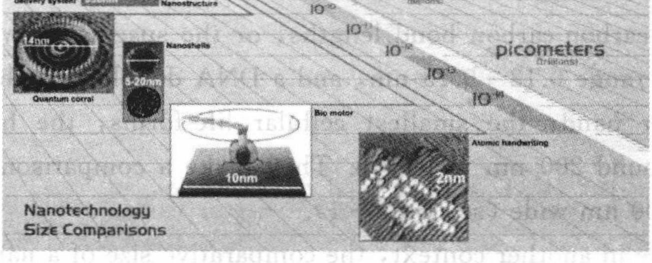


Fig.1 - 3 Size comparisons of nanometer

➢ Why people are interested in the nanoscale?

People are interested in the **nanoscale** (which we define to be **from 100 nm down to the size of atoms** (**approximately 0.2 nm**)) because it is at this scale that the properties of materials can be very different from those at a larger scale.

Their bulk properties of materials often change dramatically with nano ingredients. Composites made from particles of nano-size ceramics or metals smaller than 100 nanometers can suddenly become much stronger than predicted by existing materials-science models. For example, metals with a so-called grain size of around 10 nanometers are as much as seven times harder and tougher than their ordinary counterparts with grain sizes in the hundreds of nanometers. The causes of these drastic changes stem from the weird world of quantum physics. The bulk properties of any material are merely the average of all the quantum forces affecting all the atoms. As you make things smaller and smaller, you eventually reach a point where the averaging no longer works.

The properties of materials can be different at the nanoscale for **two main reasons**:

(1) Nanomaterials have a relatively larger surface area when compared to the same mass of material produced in a larger form. This can make materials more chemically reactive (in some cases materials that are inert in their larger form are reactive when produced in their nanoscale form), and affect their strength or electrical properties.

(2) Quantum effects can begin to dominate the behaviors of matter at the nanoscale-particularly at the lower end-affecting the optical, electrical and magnetic behaviors of materials. Materials can be produced that are nanoscale in one dimension (for example, very thin surface coatings), in two dimensions (for example, nanowires and nanotubes) or in all three dimensions (for example, nanoparticles).

1.3 Nanotechnology


Neal Lane

"If I were asked for an area of science and engineering that will most likely produce the breakthroughs of tomorrow, I would point to nanoscale science and engineering." Professor Neal Lane, Rice University, former assistant to the President for science and technology and Director of the White House Office of Science and Technology Policy.

The term "nanotechnology" was defined by Tokyo Science University professor Norio Taniguchi in a 1974 paper as follows: "'nano-technology' mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or by one molecule."

1.3.1 What is nanotechnology?

➢ So what exactly is nanotechnology?

Nanotechnology, shortened to "nanotech", **is the study of the control of matter on an**

atomic and molecular scale. Generally nanotechnology deals with structures of the size 100 **nanometers or smaller, and involves developing materials or devices within that size.** Nanotechnology is very diverse, ranging from novel extensions of conventional device physics, to completely new approaches based upon molecular self-assembly, to developing new materials with dimensions on the nanoscale, even to speculation on whether we can directly control matter on the atomic scale.

There has been much debate on the future of implications of nanotechnology. Nanotechnology has the potential to create many new materials and devices with wide-ranging applications, such as in medicine, electronics and energy production. On the other hand, nanotechnology raises many of the same issues as with any introduction of new technology, including concerns about the toxicity and environmental impact of nanomaterials and their potential effects on global economics, as well as speculation about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted. Another important criteria for the definition is the requirement that the **nanostructure** is man-made. Otherwise you would have to include every naturally formed biomolecule and material particle, in effect redefining much of chemistry and molecular biology as "nanotechnology".

The most important requirement for the nanotechnology definition is that the nano-structure has special properties that are exclusively due to its nanoscale proportions.

1.3.2 What's nanostructure?

A nanostructure is an object of intermediate (middle) size between molecular and microscopic (micrometer-sized) structures. (Note: micro-: on a small scale; macro-: on a large scale)

In describing nanostructures it is necessary to differentiate between the numbers of dimensions on the nanoscale.

(1) **One dimension** on the nanoscale, i.e., only the thickness of the surface of an object is between 0.1 nm and 100 nm.

(2) **Two dimensions** on the nanoscale, i.e., the diameter of the nanotube is between 0.1 nm and 100 nm; its length could be much greater.

(3) **Three dimensions** on the nanoscale, i.e., the spherical nanoparticles is between 0.1 nm and 100 nm in each spatial dimension. The terms nanoparticles and ultrafine particles (UFP) often are used synonymously although UFP can reach into the micrometre range.

Two main approaches are used in nanotechnology, i.e., "bottom-up" and "top-down". In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control.

Novel areas of physics such as nanoelectronics, nanomechanics and nanophotonics have been evolved during the last decades to provide a basic scientific foundation of nanotechnology.

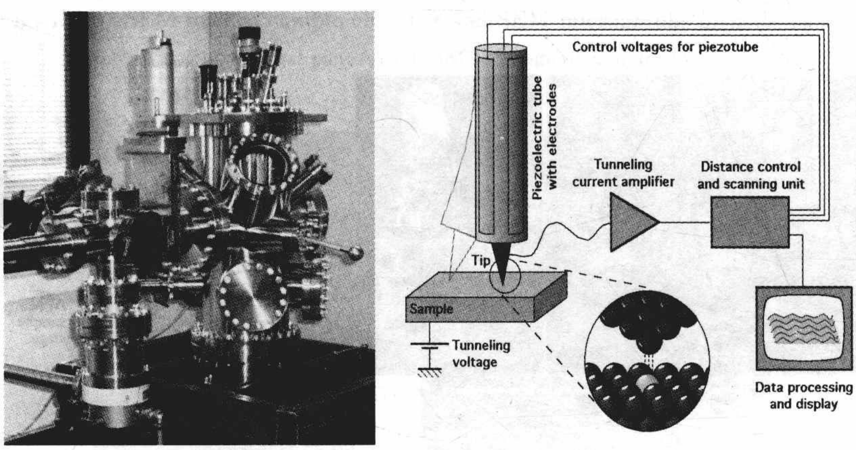
We found a good definition that is practical and unconstrained by any arbitrary size limitations:

The design, characterization production, and application of structures, devices, and systems by controlled manipulation of size and shape at the nanometer scale (atomic, molecular and macromolecular scale) that produces structures, devices, and systems with at least one novel/superior characteristic or property.

1.3.3 How to characterize in nanoscale?

➢ What tools & techniques were used?

Nanotechnology and nanoscience got started in the early **1980s** with two major developments: one is the birth of cluster science and the invention of the **scanning tunneling microscope** (STM, see Fig.1 - 4 and Fig.1 - 5). (G. Binning (left) & H. Rohrer (right), 1986 Nobel Prize). This development led to the discovery of fullerenes in 1985 and carbon nanotubes a few years later.



(a) (b)

Fig. 1 - 4 Schematic view of STM

(a)optical picture; (b)mechanism diagram

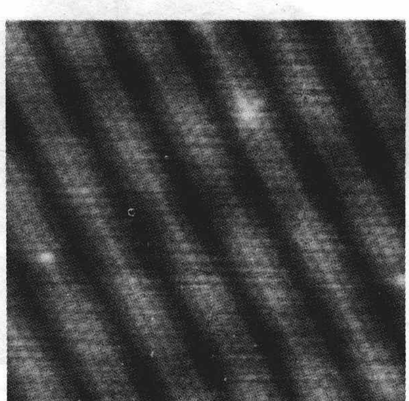


Fig. 1 - 5 ST Mmage of reconstruction on a clean Au(100) surface

There are other types of scanning probe microscopy, all flowing from the ideas of the scanning confocal microscope developed by Marvin Minsky in 1961 and the scanning acoustic microscope (SAM) developed by Calvin Quate and coworkers in the 1970s, that made it possible to see structures at the nanoscale. The tip of a scanning probe can also be used to manipulate nanostructures (a process called positional assembly). Feature-oriented scanning-positioning methodology suggested by Rostislav Lapshin appears to be a promising way to implement these nanomanipulations in automatic mode. However, this is still a slow process because of low scanning velocity of the microscope. Various techniques of nanolithography such as optical lithography, X-ray lithography, dip pen nanolithography, electron beam lithography or nanoimprint lithography were also developed. Lithography is a top-down fabrication technique where a bulk material is reduced in size to nanoscale pattern.

In another development, the synthesis and properties of semiconductor nanocrystals was studied, which led to a fast increasing number of metal and metal oxide nanoparticles and quantum dots. The atomic force microscope (AFM, see Fig.1 - 6 and Fig.1 - 7) was invented six years after the STM was invented. (1986 G. Binning, C.F. Quate & C. Gerber, Stanford University).

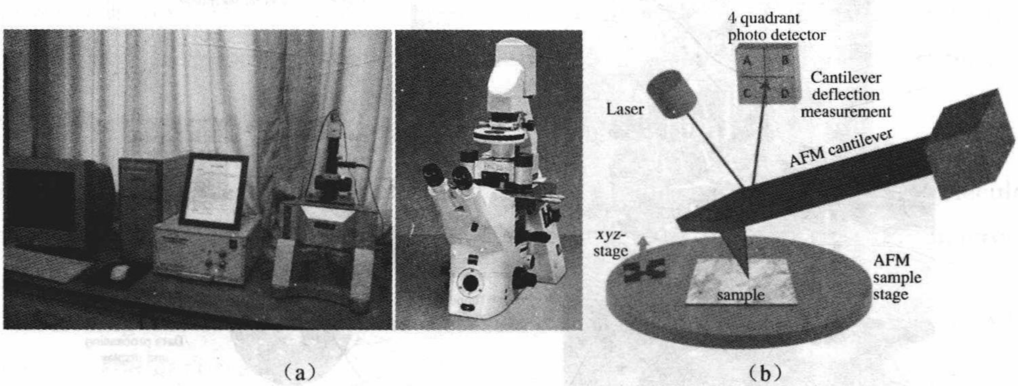


Fig. 1 - 6 Typical AFM setup

(a)optical pictures; (b)mechanism diagram

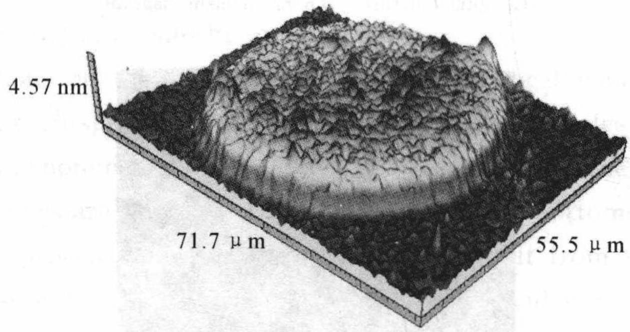


Fig. 1 - 7 3D AFM image of a DNA biochip

(1)Scanning Electron Microscope (SEM, see Fig. 1 - 8).

(2)Transmission Electron Microscope (TEM, see Fig. 1 - 9).

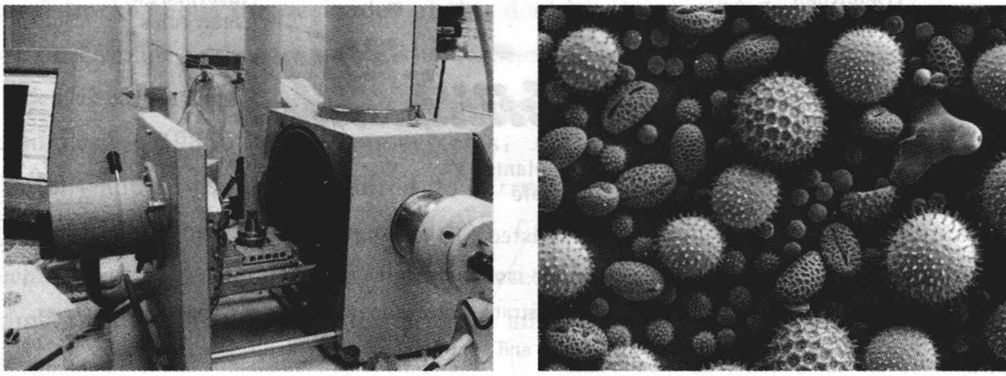
(3) Focused Ion Beam (FIB, see Fig. 1 - 10 and Fig.1 - 11).

(4) X-Ray Diffraction (XRD).

(5) Raman Spectroscopy (RS, see Fig. 1 - 12).

(6) Scanning Probe Microscopes (SPM).

(7) X-ray Photoelectron Spectroscopy (XPS).



(a) (b)

Fig. 1 - 8 SEM opened sample chamber and SEM micrographs of pollen grains

(a) optical picture; (b) SEM image of sample

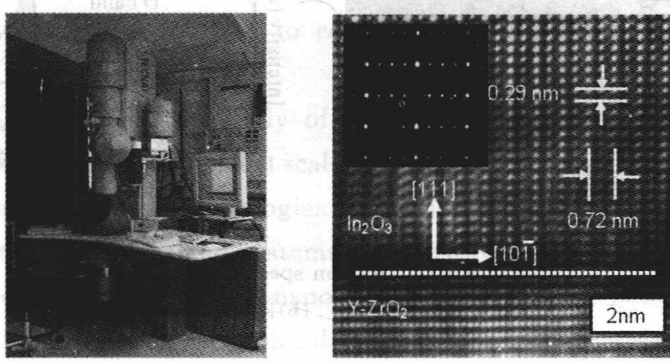
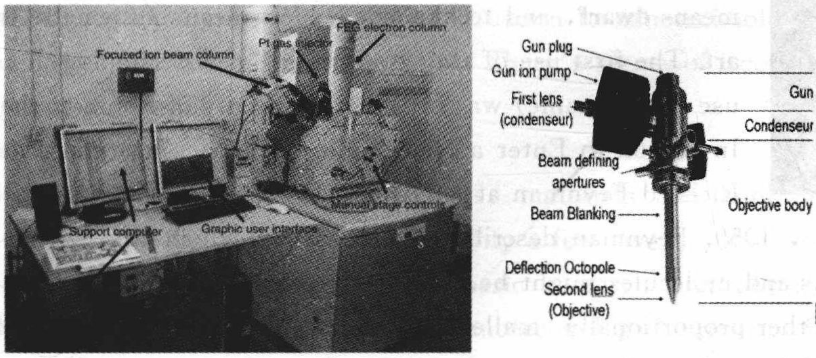


Fig. 1 - 9 Transmission electron microscope

(a) A basic TEM; (b) TEM image of Y - ZrO_2



(a) (b)

Fig. 1 - 10 Focused ion beam

(a) Optical photo of FIB facility; (b) Schematic diagram of FIB

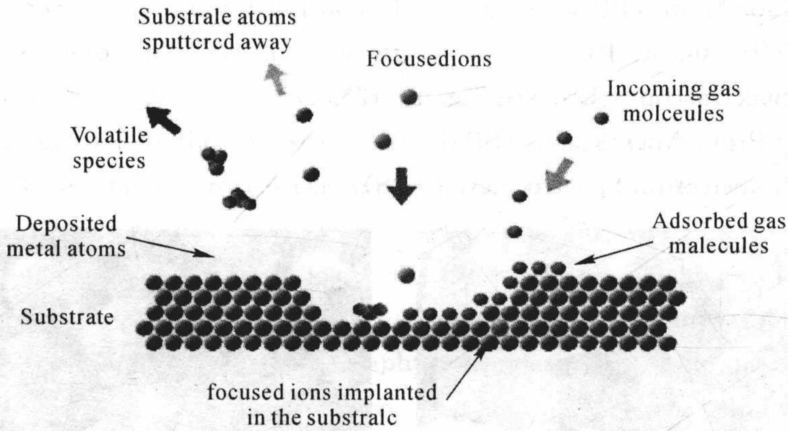
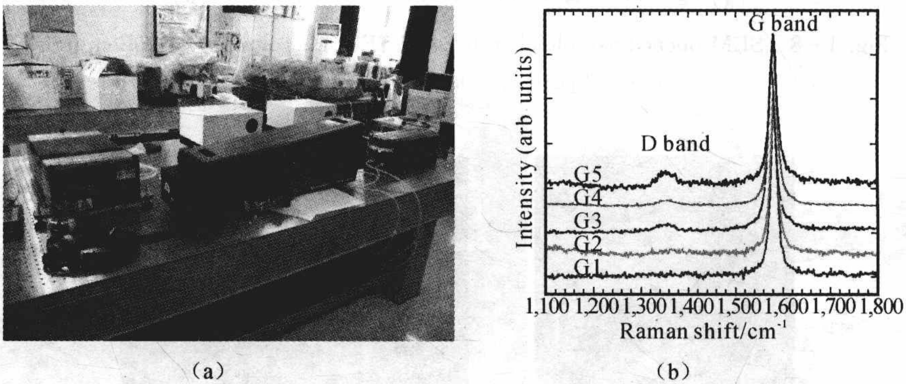


Fig. 1 - 11 Gas assisted FIB etching process

1. Adsorption of the gas molecules on the substrate.
2. Interaction of the gas molecules with the substrate. Formation of volatile and non volatile species.
3. Evaporation of volatile species and sputtening of non volatile species



(a) (b)

Fig. 1 - 12 Raman spectroscopy

(a) Typical Raman setup; (b) Raman spectrum

1.3.4 History of nanotechnology

Nanotechnology is derived from the Greek words "**nanos**", which means **dwarf**, and **technologia** which means **systematic treatment of an art.** The first use of the concepts in "nanotechnology" (but pre-dating use of that name) was in "There's Plenty of Room at the Bottom — an Invitation to Enter a New Field of Physics" a talk given by physicist Richard Feynman at an American Physical Society meeting at Caltech on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, and so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and van der

Waals attraction would become more important, etc. This basic idea appears plausible, and exponential assembly enhances it with parallelism to produce a useful quantity of end products. The term "nanotechnology" was defined by Tokyo Science University Professor Norio Taniguchi in a 1974 paper as follows: "'Nanotechnology' mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or by one molecule." In the 1980s the basic idea of this definition was explored in much more depth by Dr. K. Eric Drexler, who promoted the technological significance of nanoscale phenomena and devices through speeches and the books Engines of Creation: "The Coming Era of Nanotechnology (1986)" and nanosystems: molecular machinery, manufacturing, and computation, and so the term acquired its current sense. Engines of Creation: "The Coming Era of Nanotechnology" is considered the first book on the topic of nanotechnology. Nanotechnology and nanoscience got started in the early 1980s with two major developments: the birth of cluster science and the invention of the scanning tunneling microscope (STM). This development led to the discovery of fullerenes in 1985 and carbon nanotubes a few years later. In another development, the synthesis and properties of semiconductor nanocrystals was studied; this led to a fast increasing number of metal and metal oxide nanoparticles and quantum dots. The atomic force microscope (AFM) was invented six years after the STM was invented. In 2000, the United States National Nanotechnology Initiative was founded to coordinate federal nanotechnology research and development.

We define nanoscience as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; and nanotechnologies as the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometer scale. In some senses, nanoscience and nanotechnologies are not new. Chemists have been making polymers, which are large molecules made up of nanoscale subunits, for many decades and nanotechnologies have been used to create the tiny features on computer chips for the past 20 years. However, advances in the tools that now allow atoms and molecules to be examined and probed with great precision have enabled the expansion and development of nanoscience and nanotechnologies. Watch an introduction to nanotechnology, starting with Richard Feynman's classic talk in December 1959 "There's Plenty of Room at the Bottom—an Invitation to Enter a New Field of Physics."

➢ A word of caution.

Truly revolutionary nanotechnology products, materials and applications, such as nanorobotics, are years in the future (some say only a few years; some say many years). What qualifies as "nanotechnology" today is basic research and development that is happening in laboratories all over the world. "Nanotechnology" products that are on the market today are mostly gradually improved products (using evolutionary nanotechnology) where some form of nanotechnology enabled material (such as carbon nanotubes, nanocomposite structures or nanoparticles of a particular substance) or nanotechnology process (e. g. nanopatterning or quantum dots for medical imaging) is used in the manufacturing process. In their ongoing quest to improve existing products by creating smaller components and better performance materials, all at a lower cost, the number of companies that will manufacture "nanoproducts" (by this definition) will grow very fast and soon make up the majority of all companies across many industries. Evolutionary nanotechnology should therefore be viewed as a process that gradually will affect most companies and industries. (see Fig.1 - 13 and Fig.1 - 14)

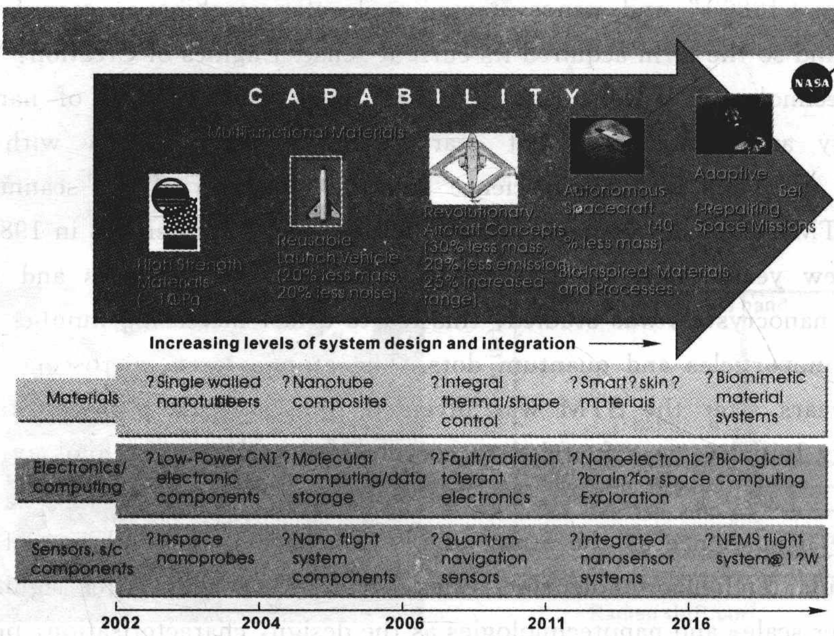


Fig. 1 - 13 NASA nanotechnology roadmap

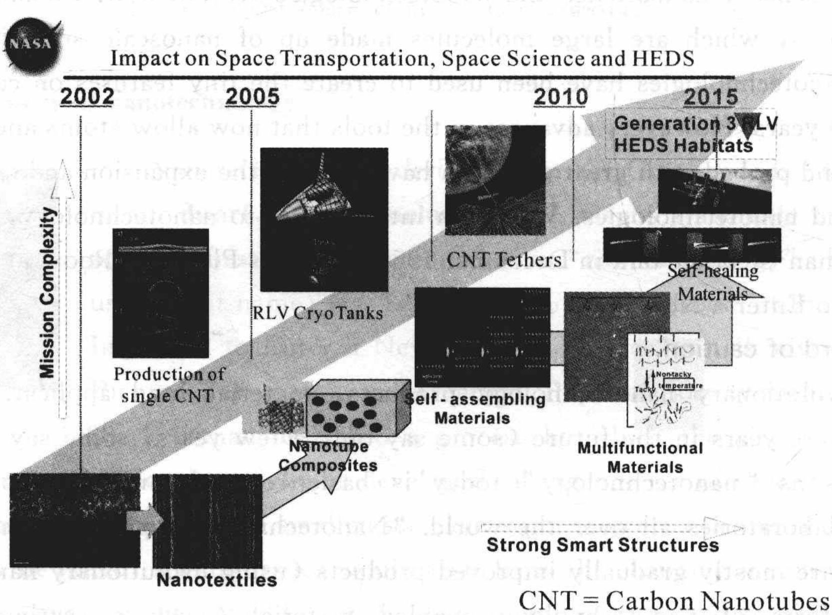


Fig. 1 - 14 Nanomaterials roadmap

1.4 Nanomaterials

An aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials which makes possible new quantum mechanical effects, for example the "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometer size range is reached. A certain number of physical properties also alter with the change from macroscopic systems. Novel mechanical properties of nanomaterials are a subject of nanomechanics research. Catalytic activities also reveal new behavior in the interaction with biomaterials.

Nanotechnology can be thought of as extensions of traditional disciplines towards the explicit consideration of these properties. Additionally, traditional disciplines can be re-interpreted as specific applications of nanotechnology. This dynamic reciprocation of ideas and concepts contributes to the modern understanding of this field. Broadly speaking, nanotechnology is the synthesis and application of ideas from science and engineering towards the understanding and production of novel materials and devices. These products generally make copious use of physical properties associated with small scales.

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); inert materials attain catalytic properties (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these unique quantum and surface phenomena that matter exhibits at the nanoscale (gold nanoparticles, AuNPs, see Fig.1 - 15). 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 was changed.

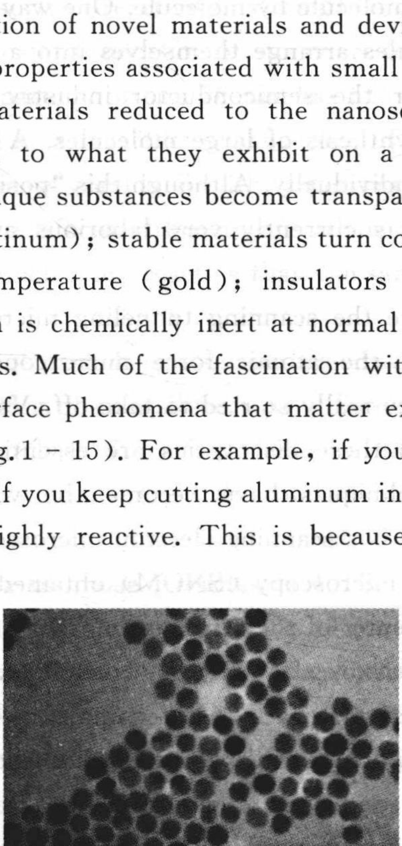


Fig.1 - 15 TEM images of AuNPs