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Nanomaterials and Devices

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PREFACE

The advent of nanotechnology is becoming an ever-visible concept in various aspects of our lives, as evident by its popular (and often incorrect) usage in advertising/marketing and entertainment. Although pop-culture references to nanotechnology are often misused or are total science fiction, its origins are derived from a rapidly growing discipline of science and engineering. Nanotechnology can be defined as the fundamental study and application of materials displaying length scales of more than 100 nm. At this size, nanoscale materials exhibit physical and chemical properties that differ greatly from those of their bulk counterparts. These interesting properties can be advantageously exploited for a number of applications and have substantial real-world impacts in fields such as medicine and those that are energy-related. Although nanotechnology research is growing rapidly throughout the world, the teaching of this subject is lacking at the university level, particularly at the first-year and second-year levels. Introducing nanotechnology earlier during the college curriculum would be of immense benefit to students and to further progress in the field. As such, the motivation in preparing this book is to introduce the concept of nanotechnology in teaching while exposing students to current nanotechnology research. Given the ever-changing nature of nanotechnology, researchers in the field need to be constantly aware of new studies to update their knowledge and to keep current. With the advent of the Internet, research data and ideas are now readily accessible and communicated to the rest of the field and serve as a plentiful source for newcomers looking to learn more about this exciting field. This can be a double-edged sword, however, because the sheer amount of information can be difficult to organize and process. Furthermore, the Internet is a nonrefereed medium and, as such, information needs to be taken with a critical viewpoint. From an educational standpoint, a major challenge is teaching students how to recognize and collect useful online resources while simultaneously instilling an intuition in the students about potentially less credible or incorrect online resources. Motivated by the facts stated here, the author felt the need for a new perspective on the progress of nanotechnology research.

Nanomaterials and related nanoscale devices constitute the core infrastructure of nanoscience and technology. With the development of nanomaterials synthesis and characterization techniques, the fundamental knowledge base has grown considerably, resulting in a thorough understanding of nanoscale properties that can be used to develop novel devices in various application areas. To this end, the major focus of this book is nanomaterials and devices. We hope this textbook will become a useful tool for students to bridge their acquired knowledge to their current or future research activities, because a major aim of this text is to prompt research into practical applications. This book references knowledge from three areas: the author's own research activities, the selected literature, and Internet resources. Regarding content selected from online resources, we have performed extensive background studies to verify that the information is correct. Additionally, we also have cited direct references to a few online resources without the original source being indicated in the reference, and for that we must apologize here and acknowledge the original authors. Our thanks are hereby extended to all the original authors who may be involved in the contents herein.

It is our desire to publish this textbook for many years to come, updating future versions with the newest trends in nanotechnology research. We thank Tsinghua University Press for their support throughout the process of writing this book.

Given the targeted readership level, the short period of preparation, and the inherent diversity within the field of nanotechnology, there may be shortcomings that are inevitable in the book. All colleagues and readers are encouraged to kindly contact the authors with your professional opinions and suggestions for new material.

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1

BASIC PROPERTIES OF NANOMATERIALS

CHAPTER OUTLINE

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In 1959, US physicist Richard Feynman, the famous Nobel Prize winner, first proposed the concept of "nanomaterials." Since then, Feynman's prediction has gradually become a reality in the development of nanoscience and nanotechnology. Peculiar physical properties of nanomaterials have a significant impact on people's lives and social development. Nanomaterials began to exhibit an increasing number of applications in sectors such as medicine, home appliances, computers and electronics, environmental protection, textile industry, machinery industry, and others.

1.1 The Nanometer and Its Brief History, Nanoscience, and Nanotechnology

Nano is the metric unit of the nanometer (nm) via transliteration. Like the millimeter and micron, the nanometer is defined as a scale of length, having no special physical meaning. Specifically, it is equivalent to one billionth of one meter (i.e., $1\ nm = 10^{-9}\ m$). One nanometer introduces a length of approximately two to three metal atoms being arranged together, or a "width" of 10 hydrogen atoms being arranged alone. A typical virus has a diameter of approximately 60–250 nm, a red blood cell has a diameter of approximately 2,000 nm, and the diameter of a hair is 30,000–50,000 nm (Figure 1.1).

Materials prefixed with "nano" can be traced back to the 1980s; it was used to define particles within a range of 1–100 nm. In July 1990, the first session of the International Symposium on Nanoscience and Nanotechnology was held

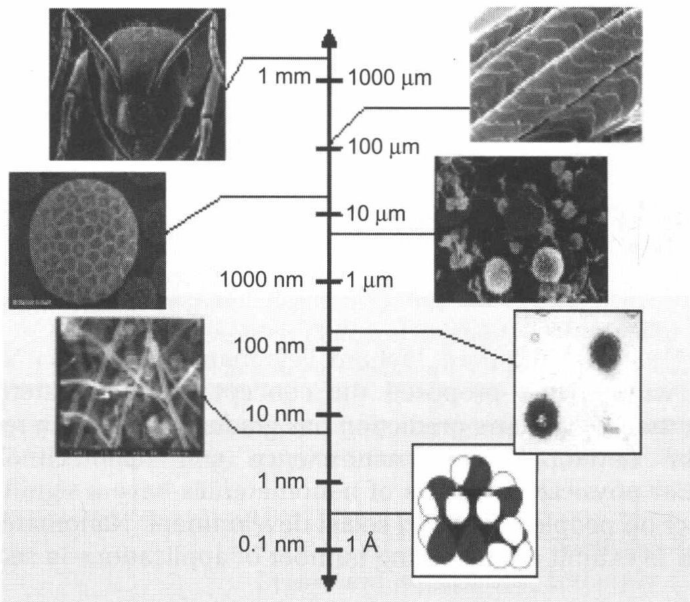

Figure 1.1 Comparison of physical scales.

in Baltimore, MD, and formally announced to the world the science of nanomaterials as a novel branch of materials science. Subsequently, a large number of scientific and technological personnel became engaged in the field of nanotechnology research, and this soon led to a "nano boom" worldwide.

In 1962, Kubo developed the quantum confinement theory on ultrafine particles, which promoted the exploration of nanoparticles in experimental physics. In 1984, the German Professor H. Gleiter and colleagues synthesized nanocrystals such as Pd, Fe, and others. In 1987, Dr. Siegel in the US-based Argonne National Laboratory prepared the nano-TiO_2 polycrystalline ceramics, which show good toughness, without any bending fracture under temperature conditions of 100°C or higher. This breakthrough brought about the first worldwide boom in nanotechnology, officially making it a branch of materials science.

As one of the most common elements in nature, the unique bonding orbital of carbon forms an abundant carbon family. People used to believe there were only three carbon allotropes in nature: diamond, graphite, and amorphous carbon. In 1985, Kroto and colleagues found the cage-like C_{60} molecules with a magic number of 60, in which 60 carbon atoms are respectively located at the top of football-shaped polyhedrons composed of 20 hexagons and 15 pentagons. By using the arc discharge of graphite electrodes, Kratschmer obtained a macro-amount of synthetic C_{60} for the very first time, triggering another wave of nanotechnology research. The later findings were a large family of spherical and spheroidal carbon allotropes.

In 1991, Professor Iljima from Japan's NEC Corporation found a hollow tube in the cathode rod with deposition of carbon black as a result of DC arc discharge in an Ar atmosphere. Under the transmission electron microscope, he found that this hollow tube had a diameter of one nanometer to tens of nanometers, and a length of tens of nanometers to one millimeter. Dozens of these tubes are structured together coaxially, leaving a radial spacing of approximately 0.34 nm between the adjacent hollow tubes, for example the plane spacing of graphite (002). This is what is now referred to as the carbon nanotube. Its unique molecular structure of a one-dimensional tube has opened a novel field in the study of one-dimensional nanomaterials. The discovery of carbon nanotubes led to another peak of nanotechnology study.

At present, nanoresearch involves three main areas: nanodevices, nanomaterials, and nanotechnology detection and characterization. The scientific significance of the research on nanostructure and nanomaterials is that it has opened a novel level of people's understanding of nature, and the subject itself has turned out to be a golden source of knowledge innovation. Nanoscale structural units (1–100 nm) are equivalent to many of the featured lengths in the substances, such as the de Broglie wavelength of electrons, the superconducting coherence length, the thickness of tunneling barriers, and the critical size of magnetic iron, thus making nanomaterials and nanostructures not only different from the microscopic atoms and molecules but also different from the macro-objects in terms of their physical and chemical properties. People's scope of exploring the nature and creating knowledge has been extended to a middle area between the macro- and micro-objects. In the field of nanotechnology, discovering novel phenomena, understanding novel laws, and developing novel concepts and theories, such activities will lay a foundation for building a scientific framework for nanomaterials. Furthermore, this also will greatly enrich the connotation of the study of nanophysics, nanochemistry, and other novel areas.

Nanotechnology renders human a mode of production and work on the nanometer scale, as well as novel tools and skills distinctively different from those in the traditional sense. For example, if we want to build robots that can enter the blood vessels, then we need to make them very small, so tools used by such robots must be made with nanomaterials. Recently, scientists have invented nanoshovels and nanospoons, which can be used by a vascular robot for operations in blood vessels. This is a typical example of nanotools.

Nanotechnology covers a wide range of contents, such as the following: the manufacturing technology of nanomaterials; the technologies of nanomaterials applied to various fields (including but not limited to high-tech fields); any device that is built in a nanoscope for double-cutting and operation of atoms and molecules; the understanding of new laws of the material transfer and energy transfer within the nanoscope; and others. So, we should not think that nanotechnology merely refers to nanomaterials, or that nanomaterials merely refer to nanopowder. Nanomaterials actually include nanofilaments, nanotubes, nanowires, nanocables, nanothin film, the three-dimensional nanoblock, composite materials, and other materials besides nanopowder. In addition, nanomaterials can be either solid or liquid. For example, there is such a thing called nanowater, which contains smaller clusters of water molecules after being processed by high-frequency ultrasound.

1.2 Characteristics of Nanomaterials

1.2.1 Perfect Law of Nanomaterials

In 1959, Feynman assumed the following: "Imagine that if one day, atoms and molecules could be arranged as what people want them to be, how different the world might be! There is no doubt that if we could control things on the very tiny scale, the scope of physical properties we can get can be greatly expanded." Now it is known that, in fact, people cannot organize atoms and molecules truly at will to form nanostructured materials, because their formation requires some special laws to be satisfied, such as the so-called perfect law of nanomaterials.

Atomic and electronic structures are commonly used to describe the structure of materials. The main parameters for atomic structure are the lattice constant, bond length, and bond angle, whereas the electronic structure has the energy band, quantum state, and distribution function as its main parameters. These parameters are constants determined for the macrosystem we are familiar with. But for the nanosystem, the majority of parameters may change as the atomic number changes. This is a typical characteristic found in materials and devices in nanotechnology that determines the diversity of nanomaterials. For the nanosystem there is an important law, and we call it the *perfect law of nanomaterials*. This can be expressed in simple language: "Existence is perfect, and only the perfect can be existent." It includes a magic number rule of nanocrystals; that is, atom clusters with the atomic numbers of 13, 55, 147, and others are considered to be stable. For example, carbon 60 and carbon 70 have the largest probability of existence in the fullerene structure, whereas structural systems such as carbon 59 or carbon 71 do not exist. That is why Smalley and colleagues [1] discovered that carbon 60 and carbon 70 exist in a number of fullerene structures and thus won the Nobel Prize. For one-dimensional nanostructures, including nanotubes and nanowires, similar rules also apply. The one-dimensional structure can be regarded as constituted by the shells, and each of the shells contains a more sophisticated structure known as a *unit*, and each unit is an atomic chain. The structure with the center containing one unit and the parcel layer containing seven units is expressed as the *7-1 structure*. If the structure also has a shell layer packaged with 11 units beyond it, then it is expressed as the *11-7-1 structure*, and so on. The 7-1 and 11-7-1 were only regarded as the most stable structures; this is called the magic number rule for the one-dimensional structure. A two-dimensional membrane is found to obey the defects melting rule; that is, it does not allow the existence of many defects. Once the defects reach a critical number, more defects will arise spontaneously and will completely destroy the two-dimensional crystalline structure. Such characteristics of low-dimensional structures are the specific interpretation of the Perfect Law.

1.2.2 Nano-Effect [2–4]

As materials are reduced to the nanometer scale—within the range of approximately 1–100 nm—the properties of the material may change abruptly so that the material may have some exceptional properties. Materials with such special properties that differ from both the original atomic or molecular components and the macroscopic material are called nanomaterials. Note that if the scale of the materials is within the nanometer range but they do not present special properties, then such materials cannot be called nanomaterials. People used to pay attention only to the microscopic objects like atoms or molecules, or to the macroscopic objects like the universe, and often overlooked this middle scope in between. Actually, a lot of materials exist within this scope in nature, except that we have never noticed the properties of physical objects of this scale before. It was Japanese scientists who took the initiative to gain a true reorganization of the performance of objects within this scale and introduced the concept of *nanotechnology*. In the 1970s, they successfully prepared advanced micro-ions by using the evaporation method and studied their performance. They found that metals such as copper and silver with electrical and thermal conductivities, after being reduced to the nanoscale, will lose their original nature and become nonconductive and nonthermal.

The same is true for magnetic materials, for example iron–cobalt alloy. When this alloy is prepared with a size of approximately 20–30 nm, the magnetic domain is changed to a single magnetic domain, exhibiting a coercivity 1,000 times higher than the original. In terms of magnetic susceptibility, nanomagnetic metal is 20 times more effective than that of ordinary metals. Its saturation magnetic moment is half that of ordinary metal. When a layer in multilayer film gets its thickness to nanosize, a giant magneto-resistive effect may occur.

Typically, $PbTiO_3$, $BaTiO_3$, and $SrTiO_3$ are ferroelectrics and can become paraelectrics when their size is reduced to nanoscale. Nanosilicon nitride ceramics are characterized by not having a typical covalent bond and being partially polarized on the interface bond with a small AC resistance. Nanoparticles prepared using inert platinum metals (platinum black) can become catalysts with excellent activity.

Changes in body surface area make the sensitivity of nanomaterials much higher than that of volume materials. Nano-optical material has unusual absorptive capacity, and nanometal presents a significantly decreased light reflection capacity: all these features are attributable to the small size and surface effects that give nanoparticles an extremely strong ability to absorb light.

Self-diffusion of Cu nanocrystals is 10^{16}- to 10^{19}-fold that of traditional crystals and is 10^{3} times more than the spread of the crystal boundary. The specific heat of nano-Cu is twice that of traditional copper. The Pd thermal expansion rate of a nanosolid is double that of a normal solid. As a heat exchanger of dilution refrigeration fluid, Ag nanocrystals can be 30% more efficient than those of traditional materials.

When crystals are reduced to nanosize, the dislocation slip is limited to the border and shows hardness that is much higher than that of volume materials. As nanocrystals, copper may have five times stronger hardness than that of the micron-scale. The fracture strength of nano-Fe crystals (6 nm) can be increased 12 times more than polycrystalline Fe.

The following is a more detailed description of nanomaterials in regard to their special nature in the optical, thermal, magnetic, mechanical, and electrical aspects.

1.2.2.1 Exceptional Optical Properties

It has long been known that scale changes of materials come with changes in color. For example, the CaSe powder in larger particles presents a red color, whereas smaller particles of CaSe powder are yellow (Figure 1.2).

When gold was differentiated down to a size less than that of light wavelengths, it would lose its original rich luster and present a black color. In fact, all the metals in the state of being ultrafine particles are shown as black. The smaller the size, the darker the color. Silver–white platinum changes into a platinum black; the metal chrome changes into a chrome black.

Ultrafine particles of metal have a very low rate of light reflection, usually less than l%. At a thickness of approximately a few microns, light can be completely eliminated. This feature can be used for highly efficient transformation of solar energy for heat and electricity and may also be used in infrared-sensitive devices or infrared stealth technology. The Gulf War

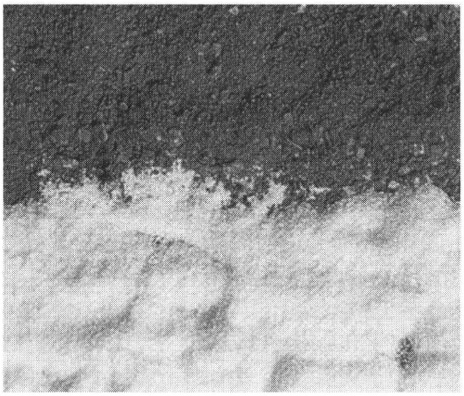

Figure 1.2 Color changes of CaSe particles of different sizes (upper: the powder in larger particles presents a red color; lower: the smaller particles are a yellow powder).

happened in the spring of 1991, and the coated materials used on the US F-117A stealth fighter contained a variety of nano-ultrafine particles, which have a strong ability to absorb electromagnetic waves of different bands. It can deceive radar to cloak the planes. The United States successfully used these fighter jets in striking important military targets in Iraq.

1.2.2.2 Exceptional Thermal Properties

A solid substance has a fixed melting point at its patterns in larger sizes, whereas this point would be significantly reduced in ultrafine forms. When particles are less than 10 nano-orders of magnitude, such decreases are particularly significant.

For example, the conventional melting point of gold is 1,064°C. When its particle size is reduced to 10 nm, the melting point will be 27°C; when the size is reduced to 2 nm, the melting point is only approximately 327°C. The conventional melting point of silver is 670°C, but that of its ultrafine particles can be less than 100°C (Figure 1.3). Therefore, the conductive paste prepared from ultrafine silver powder can be sintered at low temperatures. At this temperature level, the device substrate does not have to be high-temperature ceramic materials; instead, we can use more common materials or even plastic.

Atoms on the surface of metal nanoparticles are quite active. Powder of nanoparticles can be used as solid rocket fuel or catalyst. For example, adding 1% of aluminum or nickel ultrafine particles in rocket fuel (weight ratio) can double the combustion heat.