HANDBOOK OF NANOPHYSICS

Nanotubes and Nanowires

Edited by

Klaus D. Sattler

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Handbook of Nanophysics

Handbook of Nanophysics: Principles and Methods

Handbook of Nanophysics: Clusters and Fullerenes

Handbook of Nanophysics: Nanoparticles and Quantum Dots

Handbook of Nanophysics: Nanotubes and Nanowires

Handbook of Nanophysics: Functional Nanomaterials

Handbook of Nanophysics: Nanoelectronics and Nanophotonics

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Preface

The *Handbook of Nanophysics* is the first comprehensive reference to consider both fundamental and applied aspects of nanophysics. As a unique feature of this work, we requested contributions to be submitted in a tutorial style, which means that state-of-the-art scientific content is enriched with fundamental equations and illustrations in order to facilitate wider access to the material. In this way, the handbook should be of value to a broad readership, from scientifically interested general readers to students and professionals in materials science, solid-state physics, electrical engineering, mechanical engineering, computer science, chemistry, pharmaceutical science, biotechnology, molecular biology, biomedicine, metallurgy, and environmental engineering.

What Is Nanophysics?

Modern physical methods whose fundamentals are developed in physics laboratories have become critically important in nanoscience. Nanophysics brings together multiple disciplines, using theoretical and experimental methods to determine the physical properties of materials in the nanoscale size range (measured by millionths of a millimeter). Interesting properties include the structural, electronic, optical, and thermal behavior of nanomaterials; electrical and thermal conductivity; the forces between nanoscale objects; and the transition between classical and quantum behavior. Nanophysics has now become an independent branch of physics, simultaneously expanding into many new areas and playing a vital role in fields that were once the domain of engineering, chemical, or life sciences.

This handbook was initiated based on the idea that breakthroughs in nanotechnology require a firm grounding in the principles of nanophysics. It is intended to fulfill a dual purpose. On the one hand, it is designed to give an introduction to established fundamentals in the field of nanophysics. On the other hand, it leads the reader to the most significant recent developments in research. It provides a broad and in-depth coverage of the physics of nanoscale materials and applications. In each chapter, the aim is to offer a didactic treatment of the physics underlying the applications alongside detailed experimental results, rather than focusing on particular applications themselves.

The handbook also encourages communication across borders, aiming to connect scientists with disparate interests to begin interdisciplinary projects and incorporate the theory and methodology of other fields into their work. It is intended for readers from diverse backgrounds, from math and physics to chemistry, biology, and engineering.

The introduction to each chapter should be comprehensible to general readers. However, further reading may require familiarity with basic classical, atomic, and quantum physics. For students, there is no getting around the mathematical background necessary to learn nanophysics. You should know calculus, how to solve ordinary and partial differential equations, and have some exposure to matrices/linear algebra, complex variables, and vectors.

External Review

All chapters were extensively peer reviewed by senior scientists working in nanophysics and related areas of nanoscience. Specialists reviewed the scientific content and nonspecialists ensured that the contributions were at an appropriate technical level. For example, a physicist may have been asked to review a chapter on a biological application and a biochemist to review one on nanoelectronics.

Organization

The *Handbook of Nanophysics* consists of seven books. Chapters in the first four books (*Principles and Methods*, *Clusters and Fullerenes*, *Nanoparticles and Quantum Dots*, and *Nanotubes and Nanowires*) describe theory and methods as well as the fundamental physics of nanoscale materials and structures. Although some topics may appear somewhat specialized, they have been included given their potential to lead to better technologies. The last three books (*Functional Nanomaterials*, *Nanoelectronics and Nanophotonics*, and *Nanomedicine and Nanorobotics*) deal with the technological applications of nanophysics. The chapters are written by authors from various fields of nanoscience in order to encourage new ideas for future fundamental research.

After the first book, which covers the general principles of theory and measurements of nanoscale systems, the organization roughly follows the historical development of nanoscience. *Cluster* scientists pioneered the field in the 1980s, followed by extensive

work on *fullerenes*, *nanoparticles*, and *quantum dots* in the 1990s. Research on *nanotubes* and *nanowires* intensified in subsequent years. After much basic research, the interest in applications such as the *functions of nanomaterials* has grown. Many bottom-up and top-down techniques for nanomaterial and nanostructure generation were developed and made possible the development of *nanoelectronics* and *nanophotonics*. In recent years, real applications for *nanomedicine* and *nanorobotics* have been discovered.

Acknowledgments

Many people have contributed to this book. I would like to thank the authors whose research results and ideas are presented here. I am indebted to them for many fruitful and stimulating discussions. I would also like to thank individuals and publishers who have allowed the reproduction of their figures. For their critical reading, suggestions, and constructive criticism, I thank the referees. Many people have shared their expertise and have commented on the manuscript at various stages. I consider myself very fortunate to have been supported by Luna Han, senior editor of the Taylor & Francis Group, in the setup and progress of this work. I am also grateful to Jessica Vakili, Jill Jurgensen, Joette Lynch, and Glenon Butler for their patience and skill with handling technical issues related to publication. Finally, I would like to thank the many unnamed editorial and production staff members of Taylor & Francis for their expert work.

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Editor

Klaus D. Sattler pursued his undergraduate and master's courses at the University of Karlsruhe in Germany. He received his PhD under the guidance of Professors G. Busch and H.C. Siegmann at the Swiss Federal Institute of Technology (ETH) in Zurich, where he was among the first to study spin-polarized photoelectron emission. In 1976, he began a group for atomic cluster research at the University of Konstanz in Germany, where he built the first source for atomic clusters and led his team to pioneering discoveries such as "magic numbers" and "Coulomb explosion." He was at the University of California, Berkeley, for three years as a Heisenberg Fellow, where he initiated the first studies of atomic clusters on surfaces with a scanning tunneling microscope.

Dr. Sattler accepted a position as professor of physics at the University of Hawaii, Honolulu, in 1988. There, he initiated a research group for nanophysics, which, using scanning probe microscopy, obtained the first atomic-scale images of carbon nanotubes directly confirming the graphene network. In 1994, his group produced the first carbon nanocones. He has also studied the formation of polycyclic aromatic hydrocarbons (PAHs) and nanoparticles in hydrocarbon flames in collaboration with ETH Zurich. Other research has involved the nanopatterning of nanoparticle films, charge density waves on rotated graphene sheets, band gap studies of quantum dots, and graphene foldings. His current work focuses on novel nanomaterials and solar photocatalysis with nanoparticles for the purification of water.

Among his many accomplishments, Dr. Sattler was awarded the prestigious Walter Schottky Prize from the German Physical Society in 1983. At the University of Hawaii, he teaches courses in general physics, solid-state physics, and quantum mechanics.

In his private time, he has worked as a musical director at an avant-garde theater in Zurich, composed music for theatrical plays, and conducted several critically acclaimed musicals. He has also studied the philosophy of Vedanta. He loves to play the piano (classical, rock, and jazz) and enjoys spending time at the ocean, and with his family.

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I

Carbon Nanotubes

1

Pristine and Filled Double-Walled Carbon Nanotubes

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1.1 Introduction

As one of the most important materials in the nano area, carbon nanotubes have generated broad and interdisciplinary attention in the last two decades (Dresselhaus and Dai 2004). Their outstanding properties have been studied extensively and much effort has been devoted to their applications in areas of energy storage, electronics, sensors, and more (Baughman et al. 2002; Pengfei et al. 2003; Avouris and Chen 2006; Ajayan and Tour 2007). Research on carbon nanotubes has been primarily focused on multi-walled carbon nanotubes (MWNTs) (Iijima 1991) and single-walled carbon nanotubes (SWNTs) (Bethune et al. 1993; Iijima and Ichihashi 1993). Ever since the breakthrough of the macroscale selective synthesis of double-walled carbon nanotubes (DWNTs) (Hutchison et al. 2001), they have increasingly drawn scientific interest due to their attractive structures and properties. Strictly speaking, DWNTs are one kind of MWNTs. However, DWNTs' properties are remarkably different from those of MWNTs with three or more graphitic shells. As the intermedium between SWNTs and MWNTs, DWNTs possess the advantages of both MWNTs and SWNTs, i.e., excellent mechanical and electrical properties. More importantly, DWNTs offer lots of unique characteristics over SWNTs and MWNTs. For example, DWNTs provide simple models for the investigation of intertube interaction (Saito et al. 1993a; Zolyomi et al. 2006; Tison et al. 2008). Impressive results have been attained regarding the effects of intertube interaction on the properties of DWNTs. Furthermore, the outer tube of a DWNT can serve as a protector for the inner tube (Iakoubovskii et al. 2008). When the outer tubes are covalently functionalized, the inner tubes still retain their electronic and optical properties (Hayashi et al. 2008). Thus, the inner and outer tubes can play different roles simultaneously in electronic and optical devices.

Due to the hollow structure of carbon nanotubes, they can be filled with molecules in their interior nanometer-sized space, thus providing a new class of hybrid materials with novel structures and properties (Monthioux 2002; Kitaura and Shinohara 2006). The filling of carbon nanotubes is an effective way to modify the properties of carbon nanotubes. Interactions between carbon nanotubes and the encapsulated materials including van der Waals force, electron transfer, and orbital mixing have been shown to alter the properties of carbon nanotubes markedly. On the other hand, the spatial confinement of carbon nanotubes is expected to impart novel and distinct physical and chemical properties to the encapsulated species from their corresponding bulk samples. Carbon nanotubes are transparent to light and electron beams so that they can be used as nano test tubes or nano vessels, which also serve as a protector for the molecules that are otherwise unstable in air or could be used to study the physical and chemical properties in situ, e.g., the structure, phase transition, or chemical reactions in the nanospace, using high-resolution transmission electron microscopy (HRTEM) and optical techniques.

The filling of carbon nanotubes was primarily performed on MWNTs with the aim of fabricating nanowires using MWNTs as templates. The encapsulated materials include metals, oxides, halides, and carbides (Monthioux et al. 2006). After the macroscale synthesis of SWNTs was achieved, they attracted much

more attention because of their smaller diameters and more uniform and defect-free structures compared to MWNTs. The encapsulation of $RuCl_3$ into SWNTs by Sloan et al. (1998) and the discovery of C_{60}@SWNTs in the SWNT sample synthesized by a laser-ablation method (Smith et al. 1998) stimulated the research subject of filling of SWNTs. A large variety of molecules have been encapsulated into SWNTs, ranging from fullerenes, metallofullerenes, metal and nonmetal elements, inorganic compounds, and organic molecules (Monthioux et al. 2006). The encapsulated molecules exhibit unique properties in terms of structure, phase transition, motion behavior, and chemical properties. Meanwhile, it has been found that the electronic structure of SWNTs can be modified by dopant insertion, which makes it possible to tune the electronic properties and mechanical properties of the SWNTs. For example, arrays of C_{60} molecules nested inside SWNTs can change the local electronic structure of the SWNTs to give it a hybrid electronic band (Hornbaker et al. 2002); integrating organic molecules of electron donors or accepters into SWNTs provides stable and controllable doped SWNTs for fabricating molecular electronic devices (Takenobu et al. 2003). Doped endohedral metallofullerenes $Gd@C_{82}$ can divide a semiconducting SWNT into multiple quantum dots, where the band gap is narrowed from 0.5 eV down to 0.1 eV (Lee et al. 2002).

With regard to the encapsulation of guest molecules, DWNTs possess unique characteristics compared to SWNTs and MWNTs. On one hand, larger inner diameters of DWNTs compared to SWNTs impart the ability of accommodating large-size molecules to DWNTs. On the other hand, inner diameters of DWNTs are smaller than those of MWNTs; thus the quantum effects of the encapsulated materials are expected to be more notable in the former case. Nevertheless, there are fewer reports on the filling of DWNTs than both SWNTs and MWNTs, because the synthesis of pure DWNTs is more difficult than the synthesis of SWNTs and MWNTs. Since the successful macroscale synthesis of DWNTs (Hutchison et al. 2001), the filling of DWNTs has been drawing increasing attention.

This chapter focuses on the synthesis and properties of pristine and filled DWNTs. Section 1.2 introduces the synthesis, and structural and electronic properties of pristine DWNTs. As an important method for characterizing carbon nanotubes, features of the Raman spectra of DWNTs are also given. Section 1.3 describes DWNTs filled with fullerenes, and inorganic and organic materials. The structure, phase transition, and chemical reactions of the encapsulated species as well as the doping effects on DWNTs are discussed in detail.

1.2 Pristine Double-Walled Carbon Nanotubes

1.2.1 Synthesis of Double-Walled Carbon Nanotubes

The selective synthesis of DWNTs was first achieved by a hydrogen arc discharge method (Hutchison et al. 2001). The critical factor of this method is the use of sulfur and metals as a catalyst in the hydrogen atmosphere. From then on, large numbers of reports have emerged on the synthesis of DWNTs, which can be divided into three categories, i.e., the arc discharge method (Huang et al. 2003; Saito et al. 2003; Sugai et al. 2003; Chen et al. 2006; Qiu et al. 2006a, 2007b), chemical vapor deposition (CVD) (Ci et al. 2002, 2007; Bacsa et al. 2003; Flahaut et al. 2003; Hiraoka et al. 2003; Lyu et al. 2003; Wei et al. 2003; Zhou et al. 2003; Zhu et al. 2003; Wei et al. 2004; Li et al. 2005; Liu et al. 2005, 2007; Ramesh et al. 2005; Yamada et al. 2006; Bachmatiuk et al. 2007; Gunjishima et al. 2007; Qi et al. 2007), and the SWNT-template method (Bandow et al. 2001, 2004; Fujita et al. 2005; Guan et al. 2005b, 2008; Kalbac et al. 2005; Pfeiffer et al. 2007; Kuzmany et al. 2008; Shiozawa et al. 2008).

The arc discharge method is an effective way of producing high structural quality carbon nanotubes. MWNTs observed by Iijima using HRTEM in 1991 were by-products in an arc discharge process toward the synthesis of fullerenes. In the following years, the synthesis of carbon nanotubes using the arc discharge method was developed (Ebbesen and Ajayan 1992; Bethune et al. 1993; Iijima and Ichihashi 1993; Saito et al. 1993b; Seraphin and Zhou 1994; Journet et al. 1997). The commonly used conditions were inert atmosphere and metals (Fe, Co, Ni, etc.) used as a catalyst. In the arc discharge process, the evaporation of graphite and metals at high temperature leads to the formation of carbon nanotubes. As for the synthesis of the DWNTs, the atmosphere of hydrogen was frequently used (Saito et al. 2003; Chen et al. 2006; Qiu et al. 2006a). Another important aspect of the synthesis condition for DWNTs is the adding of sulfur to the metal catalysts or using sulfide (Huang et al. 2003; Saito et al. 2003; Chen et al. 2006; Qiu et al. 2006a). In addition, KCl was reported to behave as a promoter for the growing of DWNTs (Qiu et al. 2006a); however, the mechanism is not clear yet.

The production of carbon nanotubes by CVD is a process from gaseous carbon sources to nanotube structures catalyzed by nanoparticles. Generally, the growing conditions of SWNTs, DWNTs, and MWNTs are similar in the CVD process. In many cases, the products consist of all these kinds of carbon nanotubes. Fine control of the conditions is necessary for selectively obtaining one kind of carbon nanotubes. For the synthesis of DWNTs, catalysts reported in the literature include Fe, Co, Ni, Mo, ferrocene, sulfide, etc. Carbon sources include hydrocarbon (methane, ethene, acetylene, benzene), ethanol, etc. (Ci et al. 2002, 2007; Bacsa et al. 2003; Flahaut et al. 2003; Hiraoka et al. 2003; Lyu et al. 2003; Wei et al. 2003; Zhou et al. 2003; Zhu et al. 2003; Wei et al. 2004; Li et al. 2005; Liu et al. 2005, 2007; Ramesh et al. 2005; Yamada et al. 2006; Bachmatiuk et al. 2007; Gunjishima et al. 2007; Qi et al. 2007). One advantage of the CVD method is the facility of preparing a special assembly of DWNTs. For example, a synthesis of vertical arrays of DWNTs on flat substrates has been achieved by using catalysts with a high density (Yamada et al. 2006).

Besides the above two traditional methods, another ingenious route is taking advantage of chemical reactions of guest molecules encapsulated inside SWNTs. Bandow et al. (2001) discovered that C_{60} molecules inside SWNTs coalesce to dimers, trimers,

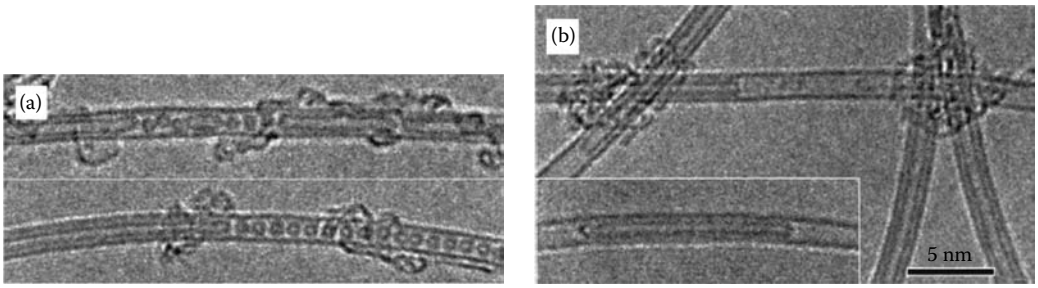

FIGURE 1.1 HRTEM images of C_{60}@SWNTs after heat treatment in vacuo (<10^{-6} Torr) at (a) 1000°C and (b) 1200°C for 14 h. (Reproduced from Bandow, S. et al., *Chem. Phys. Lett.*, 337(1–3), 48, 2001. With permission.)

and so on, and transform into tubes eventually upon heating at temperatures higher than ~800°C (Figure 1.1). Detailed Raman scattering analysis revealed that the diameters of the inner tubes derived from encapsulated C_{60} molecules are close to that of C_{60} molecules at an early stage, whereas the inner tubes turn into wider tubes that match the size of the parent SWNTs upon long-time heat treatment (Bandow et al. 2004). Kalbac et al. (2005) found that the irradiation of C_{60}@SWNTs and C_{70}@SWNTs by ultraviolet light also yields DWNTs. Molecules that can transform into carbon nanotubes inside SWNTs are not limited to fullerenes. As the research on the filling of SWNTs develops rapidly, some other kinds of molecules were found to behave similarly, including ferrocene (Guan et al. 2005b, 2008), PTCDA (Fujita et al. 2005), and $GdCp_3$ (Shiozawa et al. 2008). It was found that the diameter distributions of the inner tubes derived from C_{60} and ferrocene are different even for the same set of parent SWNTs (Pfeiffer et al. 2007).

1.2.2 Electronic Properties of Double-Walled Carbon Nanotubes

Generally, DWNTs are composed of two coaxial tubes interacting through van der Waals forces (DWNTs with an uncoaxial structure were occasionally observed [Hashimoto et al. 2005]). The electronic properties of DWNTs are determined basically by the electronic properties of the two constituent tubes. However, the interaction between the two tubes has significant effects on the electronic properties of DWNTs, which has been demonstrated by theoretical calculations (Saito et al. 1993a; Liang 2004; Song et al. 2005; Zolyomi et al. 2006, 2008; Lu and Wang 2007).

Saito et al. (1993a) investigated the effect of intertube interaction on the energy dispersion relations of DWNTs, which consist of metal–metal, metal–insulator, and insulator–metal constituents. The splitting of some energy bands induced by intertube interactions was observed (Figure 1.2). Moreover, it was predicted that metallic@metallic (M@M)-type DWNTs are still metallic and the metallic tube retains its metallic state in the case of metallic@semiconducting (M@S) and semiconducting@metallic (S@M)-type DWNTs. Liang (2004) performed calculations considering the intertube coupling strength of commensurate DWNTs as a function of the radius difference of the inner and

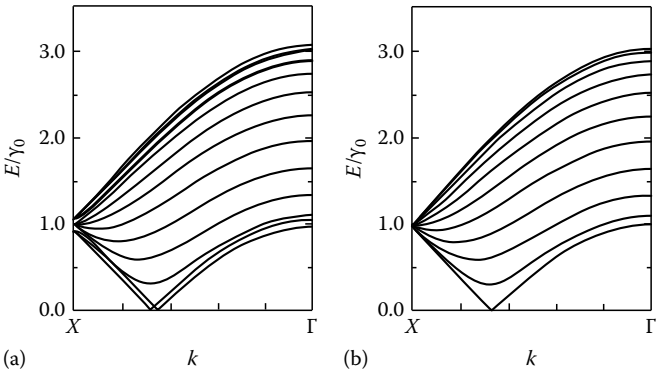

FIGURE 1.2 Energy dispersion relations of a (5, 5)@(10, 10) DWNT (a) with and (b) without considering the intertube interaction. (Reproduced from Saito, R. et al., *J. Appl. Phys.*, 73(2), 494, 1993a. With permission.)

outer tubes, i.e., $t_p = (d_g/d)t_g$, where t_p is the intertube coupling strength of DWNTs with a radius difference of d, and t_g is the interwall coupling strength of graphite with an interlayer distance of $d_g = 0.344$ nm. (If a (n_1, m_1)@(n_2, m_2) DWNT satisfies the relation $n_2/n_1 = m_2/m_1 = \lambda$, where λ is an integer, the carbon atoms in the inner tube match those in the outer tube perfectly. These kinds of DWNTs are commensurate DWNTs.) It was found that the electronic structure of semiconducting@semiconducting (S@S)-type DWNTs depends strongly on the intertube coupling strength. Specifically, strong intertube coupling tends to turn S@S type DWNTs into metallic states. Similar results were found by Moradian et al. (2007) that S@S type DWNTs become metallic when the intertube distance is small, which is attributed to the overlap of the $2p_z$ orbitals of the walls. In addition, it was revealed that the diameter of the tubes also affects the electronic properties of S@S type DWNTs (Liang 2004).

The metallic state of S@S-type DWNTs has been confirmed by experimental studies, including HRTEMs combined with $I(V)$ measurements (Kociak et al. 2002), NMR spectroscopy (Singer et al. 2005), and scanning tunneling microscopy-scanning tunneling spectroscopy (STM–STS) measurements (Tison et al. 2008). STS measurements showed evidence of the presence of a finite density of states for an individual S@S-type DWNT. Apart from the Van Hove singularities of both the inner and the outer tubes, some additional bands were observed during