

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/354181849>

Characteristics of carbon nanotubes and their nanocomposites

Chapter · January 2021

DOI: 10.1016/B978-0-12-822352-9.00011-0

CITATIONS

2

READS

924

3 authors, including:



[Piyush K. Sonkar](#)

Banaras Hindu University

72 PUBLICATIONS 1,089 CITATIONS

[SEE PROFILE](#)



[Narvadeshwar Kumar](#)

Banaras Hindu University

18 PUBLICATIONS 5 CITATIONS

[SEE PROFILE](#)

FUNDAMENTALS AND PROPERTIES OF MULTIFUNCTIONAL NANOMATERIALS

Edited by
Sabu Thomas, Nandakumar Kalarikkal,
and Ann Rose Abraham



Micro & Nano Technologies Series

PART 3: Properties of carbon-based nanomaterials

Chapter 5: Characteristics of carbon nanotubes and their nanocomposites 99

Piyush Kumar Sonkar, Narvdeswar, and Pawan Kumar Gupta

1. Introduction	99
1.1 History of carbon nanotubes.....	101
1.2 Types of carbon nanotubes	101
1.3 Physical properties of carbon nanotubes.....	102
2. Functionalization of carbon nanotubes	105
3. Characterization tool for carbon nanotubes and their nanocomposites	107
3.1 Microscopic analysis.....	107
3.2 Raman spectroscopy	111
4. Applications of carbon nanotubes and their composites.....	113
5. Summary	114
Acknowledgments.....	114
References.....	114

Chapter 6: Morphology-correlated mechanical properties of ionic liquid-modified multiwalled carbon nanotubes/poly(vinyl chloride) nanocomposites 119

Elizabeth Francis and Sabu Thomas

1. Introduction	120
2. Experimental	121
2.1 Materials and methods.....	121
3. Characterization	123
3.1 Raman spectroscopy	123
3.2 Fourier Transform Infrared spectroscopy analysis	123
3.3 Thermal analysis	123
3.4 Morphology and microstructure	123
3.5 Mechanical properties.....	124
4. Results and discussion	124
4.1 Fourier Transform Infrared spectra of nanocomposites	124
4.2 Raman spectra of nanocomposites	126
4.3 Morphology	127
4.4 Thermal properties of CN _x , CN _x (12), CN _x (16) nanocomposites.....	131
4.5 Mechanical properties of MWCNT/PVC nanocomposites.....	132
4.6 Conclusion.....	139
References.....	140

Chapter 7: Fundamentals and properties of multifunctional graphene and graphene-based nanomaterials..... 143

Srinivasarao Yarangalla and K.B. Bhavitha

1. Introduction	143
-----------------------	-----

Pawan Kumar Gupta

Pawan Kumar Gupta received B.Sc. and M.Sc. (chemistry) degrees from S.G.R. Degree College affiliated to Veer Bahadur Singh Purvanchal University, Uttar Pradesh, India. He has qualified for the CSIR-NET and GATE exams. His research interests include perovskite-based nanocomposite materials for electrochemical applications.



Amar S. Katkar

Dr. Amar S. Katkar works as an Assistant Professor in Physics at Dr. B. N. Purandare Arts, Smt. S. G. Gupta Commerce and Smt. S. A. Mithaiwala Science College, Lonavala, Maharashtra, India. He has more than 10 years of teaching experience and 15 years of research experience. He pursued a Ph.D. degree from National Tsing Hua University, Taiwan under renowned scientist Dr. Lih J. Chen (former vice-chancellor of National Tsing Hua University, Taiwan). He has more than 10 international papers published in reputed international journals. A High Impact Factor Paper award by was received by Dr. Amar S. Katkar at the Material Science and Engineering Department of National Tsing Hua University, Taiwan. He received a Research Excellence Award in 2020 by the Institute of Scholars (an ISO-certified institute by International Accurate Certification by Unified Access Service License (UASL)).



Narvdeswar

Narvdeswar received a B.Sc. (Chemistry) and M.Sc. (Physical Chemistry) from the University of Allahabad, India. He is working toward a Ph.D. in the field of mesoporous carbon-based nanocomposites and its electrochemical analysis in the Department of Chemistry, MMV, Banaras Hindu University, Varanasi, India. He has qualified for the GATE exam (India).

**Arpan Kumar Nayak**

Dr. Arpan Kumar Nayak earned an M.Sc. from Jadavpur University, India. Then, he completed a Ph.D. degree from the Materials Science Centre, Indian Institute of Technology Kharagpur (IIT-KGP), India. He was a postdoctoral fellow at Hanyang University, South Korea. Currently, he works as an Assistant Professor at the Department of Physics, School of Advanced Sciences, Vellore Institute of Technology, Vellore, India. His current research mainly focuses on the synthesis of various nanostructured materials toward environment and energy applications. He has published more than 40 articles in various international journals and two book chapters. He was assigned as the editor-in-chief of the *Journal of Applied Physics and Engineering*, *Bulletin of Scientific Research*, and *International Research Journal of Multidisciplinary Technovation*, associate editor of *Nanoscale Report*, and managing editor of the *International Journal of Materials and Product Technology* (Inderscience Publishers, I.F-0.702) (2019–21).



in teaching as a guest faculty member in the Department of Chemistry of Basanti Devi College, Ashutosh College, Gurudas College and Jadavpur University, Kolkata in 2008–14. He has worked full-time as an assistant professor at the Department of Chemistry, Bidhan Chandra College, Asansol, West Bengal (under Kazi Nazrul University) since 2015. His areas of research are coordination chemistry, catalysis, and bioinorganic chemistry.

Monica Soler

Dr. Monica Soler received her Bachelor's degree and a Master's degree in Chemistry from the University of Barcelona and her Ph.D. in Chemistry from Indiana University in 2003. She is an Associate Professor at the Department of Chemical Engineering, Biotechnology, and Materials at the University of Chile. Her group is engaged in the design and synthesis of curcuminoid molecules and the preparation of functionalized materials and metal-organic frameworks for the detection of contaminants.



Piyush K. Sonkar

Dr. Piyush Kumar Sonkar received a B.Sc. (Chemistry), M.Sc. (Inorganic Chemistry), and Ph.D. (Chemistry) from Banaras Hindu University, India. He qualified in the CSIR-UGC-NET exam and GATE (India). After completing a Ph.D., he has continued research at the Department of Chemistry, MMV, Banaras Hindu University, Varanasi, India. His research interests include electrocatalysis of carbon-based nanocomposites, metal-organic frameworks, and silica materials for electrochemical energy storage and sensing applications.



Characteristics of carbon nanotubes and their nanocomposites

Piyush Kumar Sonkar, Narvdeswar, Pawan Kumar Gupta

Department of Chemistry, MMV, Banaras Hindu University, Varanasi, Uttar Pradesh, India

Chapter Outline

1. Introduction 99

- 1.1 History of carbon nanotubes 101
- 1.2 Types of carbon nanotubes 101
- 1.3 Physical properties of carbon nanotubes 102
 - 1.3.1 Electrical conductivity 103
 - 1.3.2 Mechanical properties 104
 - 1.3.3 Thermal properties of carbon nanotubes 104

2. Functionalization of carbon nanotubes 105

3. Characterization tool for carbon nanotubes and their nanocomposites 107

- 3.1 Microscopic analysis 107
- 3.2 Raman spectroscopy 111

4. Applications of carbon nanotubes and their composites 113

5. Summary 114

Acknowledgments 114

References 114

1. Introduction

The carbon atom is one of the important elements in the periodic table. It can form sp^3 , sp^2 , and sp hybridizations [1–3]. There are different allotropes of carbon based on its arrangements, such as diamond, graphite, graphene, carbon nanotubes (CNTs), and fullerene [3]. These allotropes have a wide variety of physical and chemical properties [1–4]. Diamond is made of sp^3 -hybridized carbons arranged in a tetrahedral lattice. On the other hand, graphite has a planar arrangement of sp^2 -hybridized carbons [3,5]. The sheaths of the graphite are attached only by van der Waals interactions. Because of this structural arrangement, graphite is softer than diamonds [5]. A single layer of graphite is known as graphene. Buckminster fullerene, commonly known as fullerene, has a spheroidal

arrangement like graphene [6,7]. The structures of different allotropes of carbon are shown in Fig. 5.1. Among these allotropes, CNTs are one of the most important members of carbon. It is the most exciting addition of the carbon family. CNTs lie between fullerenes and graphite as a new member of carbon allotropes. CNTs have a nanometer-sized diameter and a length of up to several micrometers [1–4]. A rolled structure of the graphite sheath is called CNTs. It is arranged in a hexagonal pattern with an arrangement similar to that of the structure of graphite [8,9]. CNTs are considered to be a graphitic cylinder 1 nm in diameter closed at the ends with caps containing carbon pentagons and hexagons. They can be either semiconducting or metallic [10,11]. CNTs have high electrical conductivity, chemical stability, a surface area, and high thermal stability [11]. They have a variety of applications in the fields of physical science, material science, biological science, pharmaceuticals,

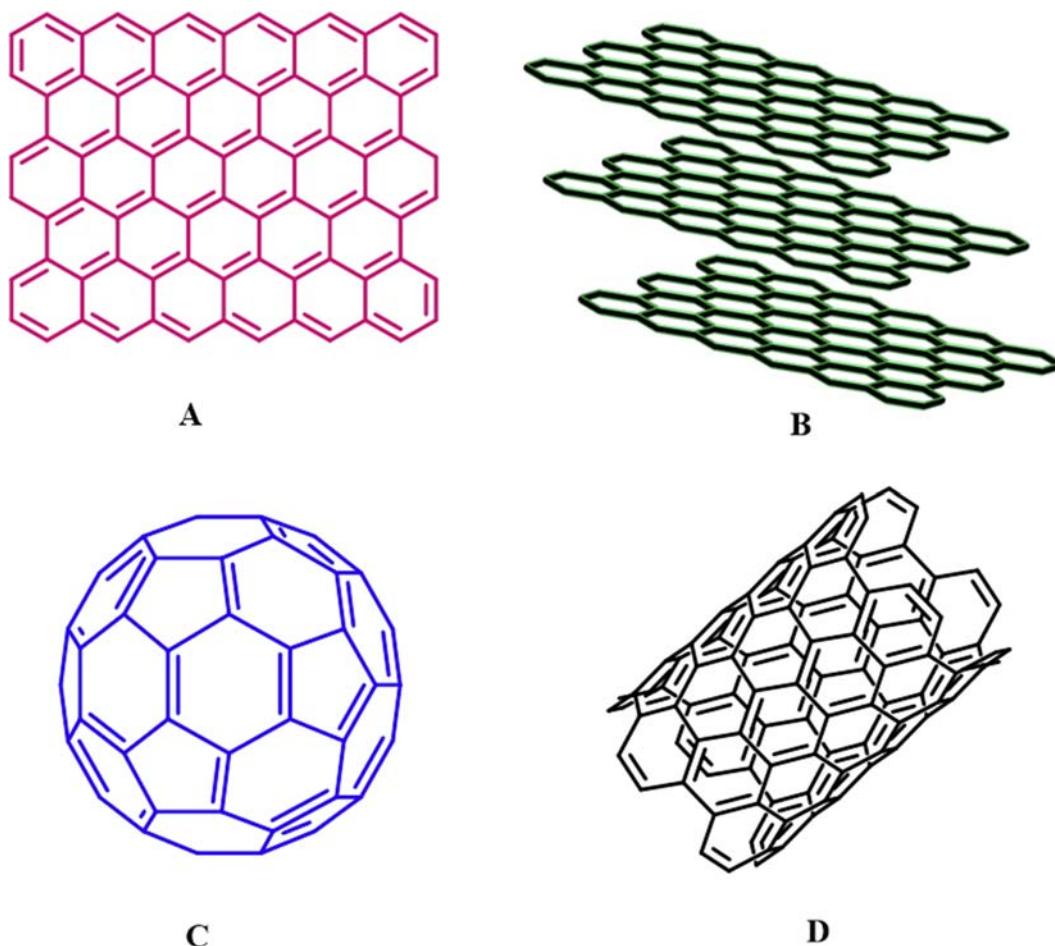


Figure 5.1

Different types of carbon allotropes (A–D) and their crystallographic arrangements: (A) graphene, (B) graphite, (C) fullerene, and (D) carbon nanotubes.

medicine, drug development, and so on [11–13]. They can be used in diodes, supercapacitors, medicine, electrocatalysts, nanocomposites, catalyst supports, and more [6,13,14]. They are also used as an electrocatalytic support material for the development of electrochemical sensors for toxic chemicals, pesticides, pollutants, drugs, and so forth [4,6,15]. In this chapter, the characteristics of CNTs and their nanocomposites, characterization tools, and applications are briefly discussed.

1.1 History of carbon nanotubes

The discovery of CNTs has created controversy in the scientific community. The most cited research articles suggest that CNTs were first discovered by Japanese scientist Sumio Iijima in 1991 [3,16,17]. However, some evidence supports the discovery of CNTs before Iijima's report [3,18]. More recent investigations indicate the discovery of multiwalled carbon nanotubes (MWCNTs) in the early 1950s. The discovery of hollow carbon filament (with a diameter as high as the nanometer range) in 1952 provides support for the discovery of MWCNTs in the early 1950s [18]. The systematic study of Iijima was significant for the discovery of MWCNTs, but we cannot neglect the earlier scientific contributions. On the other hand, single-walled carbon nanotubes (SWCNTs) were first reported independently by Iijima and Ichihashi [19] and by Bethune et al. [20]. The discovery of SWCNTs is more fundamental than MWCNTs. It has a significant number of theoretical predictions and interpretations. After the discovery of CNTs, scientists explored the characteristics, properties, and applications of CNTs. The most important progress in the field of CNTs and its nanocomposites is discussed in the following sections.

1.2 Types of carbon nanotubes

CNTs are categorized based on the orientation of the graphene sheath. There are three types of CNTs: chiral (n,m), zigzag ($n,0$), and armchair (n,n), where m and n are an integer value between two extremes for chiral vector C [3,17,21]. Two atoms in a planar graphene sheath are chosen and one is used as the origin. Vector C points the first atom toward the second one, as is shown in Fig. 5.2 [21]. These arrangements of carbon atom in CNTs may behave as metallic or semiconducting. These special characteristics of CNTs open up new dimensions for the development of functional materials [12].

Based on the number of concentric cylinders, CNTs are classified into different categories: SWCNTs, double-walled carbon nanotubes, triple-walled carbon nanotubes, and MWCNTs [11,22]. The schematic structures of SWCNTs and MWCNTs are shown in Fig. 5.3 [3]. In SWCNTs, the thickness of the cylindrical layer is 0.2–2 nm and the length is up to several micrometers. The structures of SWCNTs are conceptualized by wrapping a single layer of graphene into a cylinder. The exceptional electronic properties of SWCNTs make them outstanding compared with other forms of CNTs [23,24]. On the other hand,

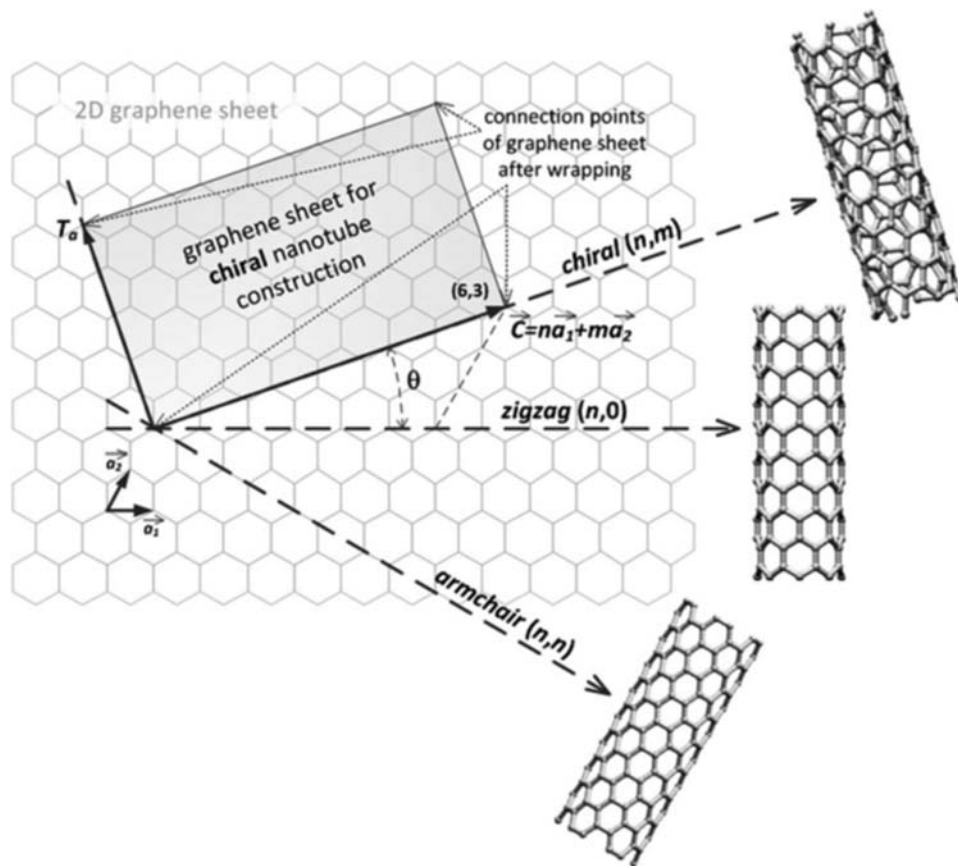


Figure 5.2

Growth of carbon nanotubes from graphene sheath along with chiral vector C . Reproduced with permission from J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam, R. Kizek, *Methods for carbon nanotubes synthesis*, *J. Mater. Chem.* 21 (2011) 15872–15884.

the inner diameter of MWCNTs ranges from 1 to 3 nm and the outer diameter is 2–100 nm [3,25]. The inner diameter of MWCNTs is wider than that of SWCNTs. MWCNTs have a tube-like structure with multiple layers of graphite rolled to form a tube-like arrangement [25].

1.3 Physical properties of carbon nanotubes

CNTs have unique structural, electrical, and mechanical properties that make them an outstanding and attractive material for researchers [26,27]. The excellent mechanical properties, exceptionally high-tensile strength, and stiffness have stimulated interest and promoted research with CNTs [26,28]. These properties make the CNTs suitable for high-

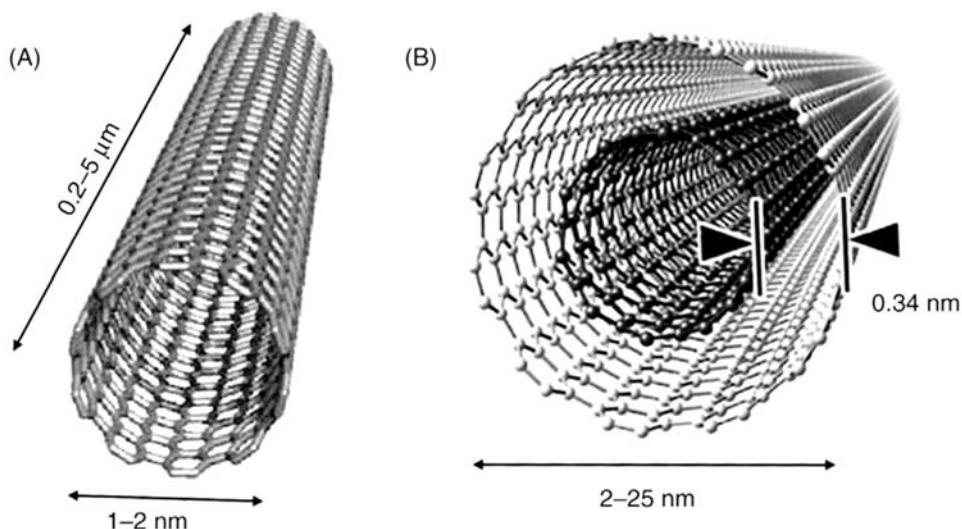


Figure 5.3

Structure of (A) single-walled carbon nanotubes and (B) multiwalled carbon nanotubes with a representation of their dimensions. *Reproduced with permission from R. Ghasempour, H. Narej, CNT Basics and Characteristics, Carbon Nanotube-Reinforced Polymers, Elsevier (2018) 1–24.*

performance structure materials, electromagnetic interference shielding, wave absorption, optical limiting, supercapacitors, and polymer-based light-emitting devices [26–28].

1.3.1 Electrical conductivity

CNTs have outstanding electronic properties. They have a nanometer diameter and a symmetric structure of two-dimensional (2D) graphene sheet that provides extraordinary electronic conduction of a 1D CNT structure [28]. Theoretical calculations and experimental measurements show conducting features of SWCNTs as quantum wires, CNTs bundles, and conduction in MWCNTs [3,29]. Theories regarding the electronic properties of SWCNTs suggest that the conductivity of SWCNTs is influenced by the helicity of tubes and their diameter. It depends on the indices (n,m) [30]. The electrical conductivity of SWCNTs and MWCNTs lies in the range 10^2 – 10^6 and 10^3 – 10^5 S/m, respectively [8,28,31–33]. The exceptional electronic properties and nanotube structure of CNTs provide significant applications in nanoelectronics. The diameter-influenced energy gap of CNTs provide special characteristics as a semiconducting material [34]. In addition, SWCNTs are used in field-effect transistors, which have a huge advantage over conventional transistors. The 1D nature of SWCNTs make them a key component in a single-electron transistors. The high electronic conductivity of SWCNTs make them a useful material for memory devices [34].

1.3.2 Mechanical properties

The mechanical strength of CNTs is highly influenced by the distribution and types of defects present in nanotubes [26]. These defects also affect the thermal and electrical properties. Different synthesis processes such as laser ablation, arc generation, and chemical vapor deposition (CVD) modulate the nature of the defects in the CNTs [26]. The mechanical strength of CNTs is measured in terms of the tensile strength. It is a difficult task to measure the tensile strength of CNTs. Yu et al. measured the tensile strength of SWCNT bundles varying from 13 to 52 GPa [35]. The tensile strength of the MWCNTs measured by Yu et al. ranged from 11 to 63 GPa [36]. Furthermore, the tensile strength of MWCNTs prepared by CVD was measured by Pan et al.; they reported a low tensile strength of 1.72 ± 0.64 GPa [37]. Generally, prepared CNTs are not a single SWCNT or MWCNTs. Initially, they may be either agglomerated SWCNTs or MWCNT bundles [38]. The high tensile strength and stiffness of a single SWCNT may not be the same in the CNT nanostructure. The high tensile strength, stiffness, tensile load, and lower density indicate the extraordinary mechanical properties of the CNTs. Hence, it is useful for developing strong composite materials.

1.3.3 Thermal properties of carbon nanotubes

The thermal conductivity and thermal expansion of the CNT are significant properties owing to its fundamental and technical importance. The small size and unique configuration directly affect the thermal behavior of CNTs [27,39]. Because of these special characteristics, CNTs may be considered an ideal material for the thermal management and investigation of low-dimensional phonon physics. Pyrolytic graphite represents high in-plane thermal conductivity. However, type II-a diamond represents extremely high thermal conductivity [39]. The thermal conductivity of graphite across the plane is extremely low because of the weak interaction of van der Waals forces. According to molecular dynamics and experimental studies, the thermal conductivity of single or bundled SWCNTs and MWCNTs are 20–6000 W/mK [40]. The thermal conductivity of a single MWCNT measured by Samani et al. is 2586 W/mK [40]. The outstanding mechanical, thermal, and electrical properties of the CNTs are useful for developing various electronic devices and composite materials. The general physical properties of the SWCNTs and MWCNTs are summarized in Table 5.1 [8,28,31–33].

The formation of CNT composites with epoxy enhances thermal conductivity 6 to 10 times higher. Gardea et al. reported increased electrical and thermal conductivity owing to the formation of CNT–epoxy composite materials [34]. It is well-documented in the literature that electrical, thermal, and mechanical properties can be enhanced owing to the formation of an appropriate composite of CNTs: for example CNT–bismaleimide composites [41], polyamide–MWCNT nanocomposites [42], polyimide–CNTs fabricated by in situ polymerization [43], MWCNTs and epoxy composites [44], well-dispersed

Table 5.1: Physical characteristic of single-walled carbon nanotube (SWCNTs) and multiwalled carbon nanotube (MWCNTs).

Characteristics	MWCNTs	SWCNTs
Nanotube diameter	0.2–2 nm	2–100 nm
Nanotube length	Up to several micrometers	Up to several micrometers
Concentric nanotubes, n	More than 2	1
Specific area	$(0.4\text{--}0.9) \times 10^3 \text{ m}^2/\text{g}$	$(0.2\text{--}0.4) \times 10^3 \text{ m}^2/\text{g}$
Conductivity (thermal)	$(3\text{--}6) \times 10^3/\text{Wm/K}$	$(2\text{--}3) \times 10^3/\text{Wm/K}$
Bulk specific gravity	$0.8\text{--}1.3 \text{ gcm}^{-3}$	$1.8\text{--}2.6 \text{ gcm}^{-3}$
Young's modulus	$\sim 1.0 \text{ kPa}$	$\sim 1.0 \text{ kPa}$
Conductivity (electrical)	$(1\text{--}10,000) \times 10^2 \text{ Scm}^{-1}$	$(1\text{--}100) \times 10^3 \text{ Scm}^{-1}$
Specific surface area	$(4\text{--}9) \times 10^2 \text{ m}^2/\text{g}$	$(2\text{--}4) \times 10^2 \text{ m}^2/\text{g}$
Stability (thermal) in air	550–650°C	550–650°C

Data for the characteristics of CNTs were taken from Ghasempour and Narei [3], Cao et al. [8], Meyyappan [28], Xie et al. [31], Ma et al. [32], and Díaz et al. [33].

SWCNT–polystyrene composites [45], MWCNT-reinforced carbon matrix composites [46], polybenzimidazole with CNT–graphene oxide hybrids [47], CNT-reinforced Al matrix composites [48], and so forth [49–51].

2. Functionalization of carbon nanotubes

The properties of CNTs can be enhanced by the insertion of unique functional groups. Two main are used for the functionalization of CNTs: noncovalent and covalent functionalization [52–54]. This functionalization of CNTs was carried out using different chemical functional groups and molecules. In the noncovalent functionalization of CNTs, aromatics, peptides, polymers, nucleic acids, surfactants, and oligomers were bound to CNTs with noncovalent interactions [52,55]. Noncovalent interactions include several aspects such as van der Waals forces, hydrophobic interaction, and π -stacking [54]. According to some reports, the electrical conductivity and aromatic structure of CNTs can be retained during noncovalent functionalization [6,9]. Without doubt, the noncovalent interactions provide weak strength to CNTs, which makes them unstable or less stable functionalized moieties [54].

In covalent functionalization; CNTs can be functionalized from ends, defects and side walls. The ends and defects method have high specificity for the reactions compare to side walls [56–58]. Functionalized CNTs can be prepared by covalent bonding between the surfaces of CNTs and compatible functional groups. In these ways, the surface of CNTs has been functionalized by different methods [57,58]. These variations provide a suitable platform for the functionalization of CNTs. During functionalization, the side walls of CNTs are damaged and increase the other features of CNTs. CNTs can be functionalized

with concentrated sulfuric acid and nitric acid treatment [56,59]. Treatment of these acids provides the carboxylic group at the point defect of the carbon skeleton. Carboxylic acid functional groups increase the hydrophilicity of CNTs [59]. Hence, because of the covalent functionalization of the carboxylic acid group, CNTs become more water-soluble [56]. In addition, stable CNTs functionalization can be prepared by covalent bonding or coupling, which makes it more appropriate for drug delivery [58]. Different types of CNTs functionalization are summarized in Fig. 5.4 [60].

Different types of CNT functionalization are available in the literature: for example, electrochemical functionalization of SWCNTs with phosphorus and nitrogen species [61], MWCNTs functionalized with bathocuproinedisulfonic acid [62], organic functionalization of CNTs [63], sidewall functionalization of CNTs [64], CNT functionalization using a silane coupling agent [65], functionalization of CNTs with polystyrene, functionalization of CNTs with amines and enzymes [66], and so on [58,67–69]. Large numbers of CNT functionalized composites have been documented in the literature [58,70,71]. These functionalized CNTs and composite materials are useful in various applications such as electrochemical energy storage, sensing, material development, drug delivery, and pharmaceuticals [7,12,14,28].

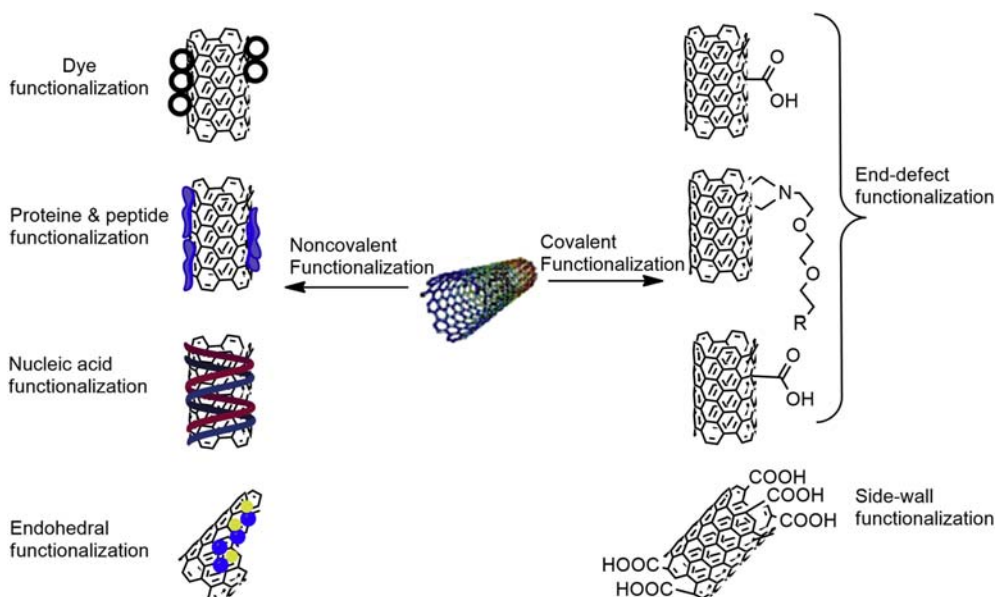


Figure 5.4

Covalent and noncovalent functionalization of carbon nanotubes. Reproduced with permission from B. Singh, S. Lohan, P.S. Sandhu, A. Jain, S.K. Mehta, *Functionalized Carbon Nanotubes and Their Promising Applications in Therapeutics and Diagnostics, Nanobiomaterials in Medical Imaging*, Elsevier (2016) 455–478.

3. Characterization tool for carbon nanotubes and their nanocomposites

The general physical properties of CNTs were discussed earlier in this chapter. However, CNTs and their composites can be characterized using spectroscopic and microscopic methods. A brief discussion is provided here for microscopic characterization using a scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive X-ray analysis (EDAX), EDAX mapping, and atomic force microscope (AFM). In the spectroscopic methods, we will discuss only Raman spectroscopy for the characterization of CNTs and their composites. The other spectroscopic and characterization methods are beyond the scope of this chapter.

3.1 Microscopic analysis

SEM analysis is an important tools for characterizing CNTs and their composite materials. SEM images of SWCNTs and MWCNTs generally appear as fibers. The appearance of the fibrous bundle indicates the CNTs. Any small change in the tubular structure can be identified using this technique. SEM images of the SWCNTs and MWCNTs are shown in Fig. 5.5 [72,73]. The structure of SWCNTs (A) and MWCNTs (B) is clearly tubular in the SEM image.

The SEM images of the CNTs show the clear appearance of the nanotubes [72,73]. However, TEM analysis shows the high-resolution images. Even the layers of CNTs can also be visible in high-resolution TEM images. The TEM images of SWCNTs and

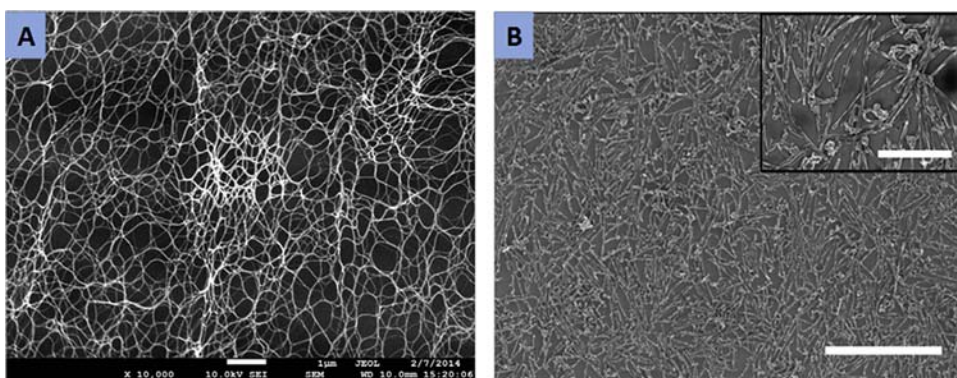


Figure 5.5

Scanning electron microscope image of (A) single-walled carbon nanotubes and (B) multiwalled carbon nanotubes. Reproduced with permission from A. Tonkikh, V. Tsebro, E. Obratsova, K. Suenaga, H. Kataura, A. Nasibulin, E. Kauppinen, E. Obratsova, Metallization of single-wall carbon nanotube thin films induced by gas phase iodination, *Carbon*, 94 (2015) 768–774, K. Kedzierski, K. Rytel, B. Barszcz, A. Gronostaj, Ł. Majchrzycki, D. Wróbel, Unusual conductivity temperature dependence of multiwalled carbon nanotube thin film, *Chem. Phys. Lett.*, 712 (2018) 144–148, respectively.

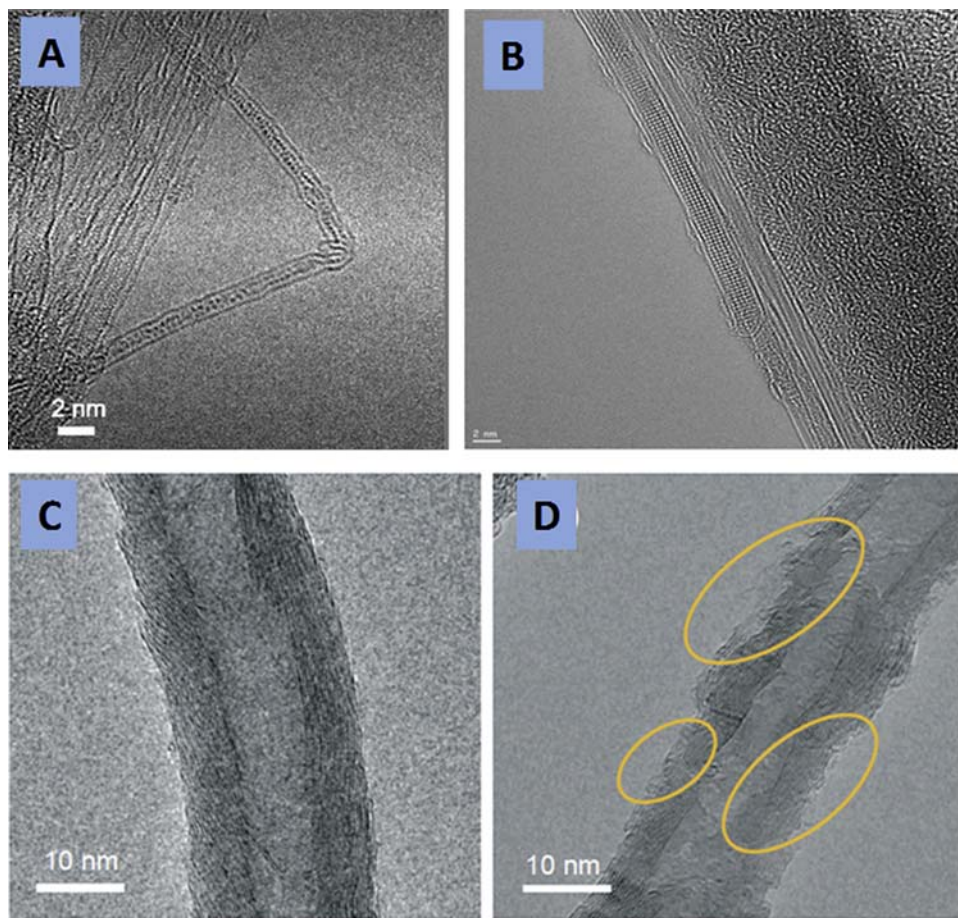


Figure 5.6

Transmission electron microscope images of single-walled carbon nanotubes filled with iodine from a gas phase at different magnification (A, B) and acid-purified multiwalled carbon nanotube (MWCNTs) (C) and acid-functionalized MWCNTs (D). The circle in (D) represents the rupture of the tube wall owing to acid functionalization. *Reproduced with permission from A.*

Tonkikh, V. Tsebro, E. Obratsova, K. Suenaga, H. Kataura, A. Nasibulin, E. Kauppinen, E. Obratsova, Metallization of single-wall carbon nanotube thin films induced by gas phase iodination, Carbon, 94 (2015) 768–774, S. Sweeney, S. Hu, P. Ruenaroengsak, S. Chen, A. Gow, S. Schwander, J.J. Zhang, K.F. Chung, M.P. Ryan, A.E. Porter, Carboxylation of multiwalled carbon nanotubes reduces their toxicity in primary human alveolar macrophages, Environ. Sci. Nano 3 (2016) 1340–1350 respectively.

MWCNTs are shown in Fig. 5.6 [72,74]. Generally, composites of CNTs represent some nodules with dark shading of layering on the nanotubes [9,75]. Modification of CNTs with functional groups, enzymes, biomolecules, drugs, or other moieties can be identified with the help of SEM and TEM analysis [10,72,73].

In addition, EDAX and EDAX mapping also provide support to these characterization tools [4,6]. The EDAX technique provides the presence of elements in the samples. EDAX coupled with SEM or TEM enables elemental identification of selected regions in the microscopic images [76]. The EDAX spectra of the SWCNTs and MWCNTs show the presence of carbon and oxygen atoms in the elemental composition [4,9]. The incorporation of any functional groups or foreign molecules on the CNTs can easily be identified with this technique.

The characterization of CNTs and their composites are generally performed with the collective interpretation of these techniques. For example, nickel salophen immobilized MWCNTs are shown in Fig. 5.7 [4].

Here, incorporation of nickel salophen was visible in the SEM and TEM images in the form of the dark lining and spots. In addition, the presence of nickel salophen was identified using the EDAX study. EDAX shows the presence of nickel as an indication of nickel salophen [4].

The elemental distribution of the constituent elements of CNTs and their composites can be visualized using EDAX mapping. Fig. 5.8 shows EDAX and EDAX mapping of

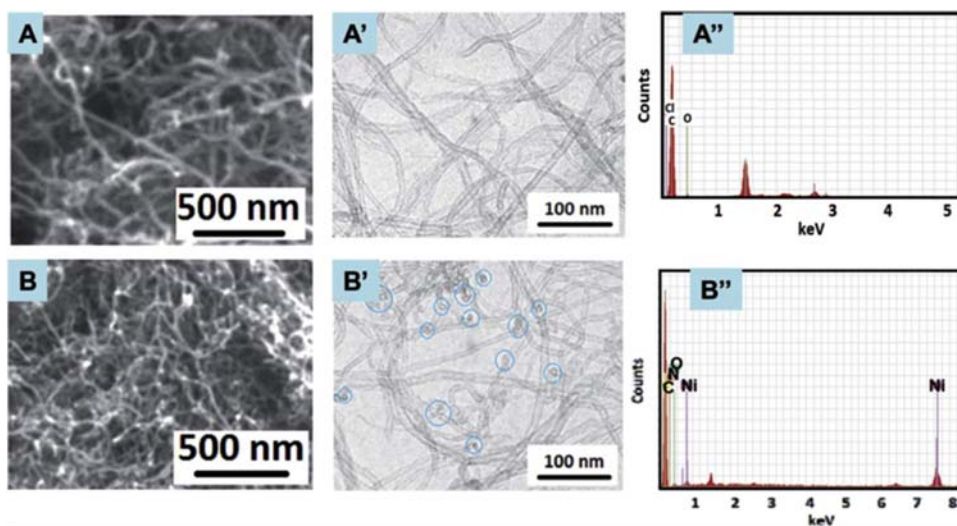


Figure 5.7

(A, B) Scanning electron microscope images, (A', B') transmission electron microscope images showing the morphology, and (A'', B'') energy dispersive X-ray analysis of (A, A', and A'') multi-walled carbon nanotubes (MWCNTs) and (B, B', and B'') MWCNT–nickel salophen composite. Reproduced with permission from P.K. Sonkar, V. Ganesan, S.A. John, D.K. Yadav, R. Gupta, *Non-enzymatic electrochemical sensing platform based on metal complex immobilized carbon nanotubes for glucose determination*, RSC Adv. 6 (2016) 107094–107103.

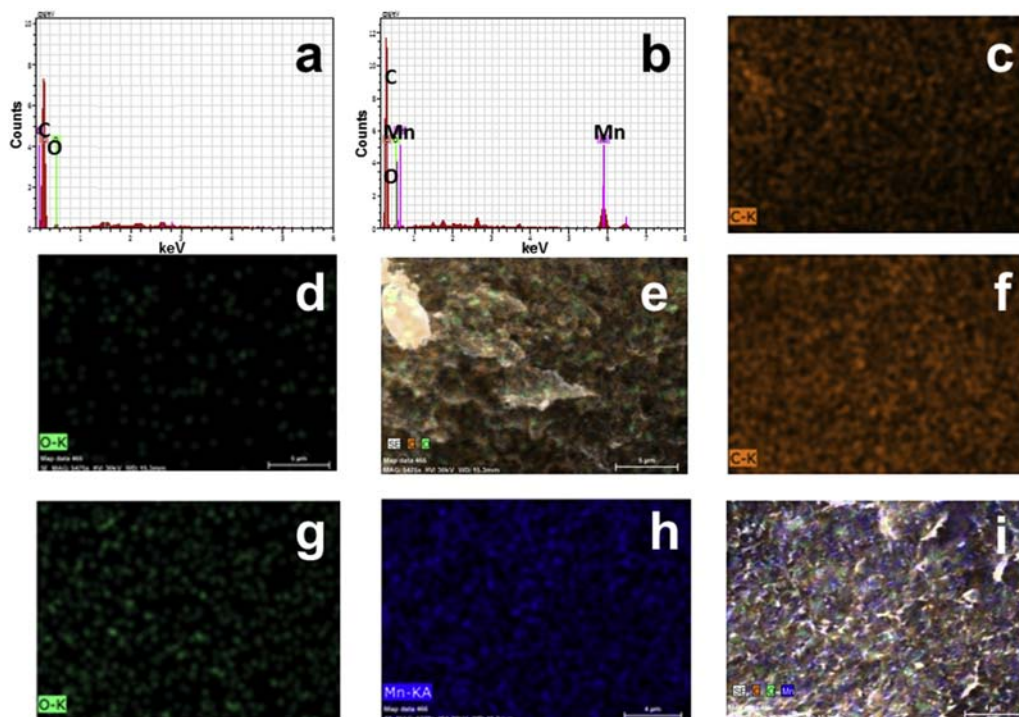


Figure 5.8

Energy dispersive X-ray analysis (EDAX) spectra of (A) multiwalled carbon nanotube (MWCNTs) and (B) MWCNT-manganese salen composite. (C–I) EDAX mapping of MWCNTs. (F–I) MWCNT-manganese salen composite. *Reproduced with permission from P.K. Sonkar, V. Ganesan, S.K. Sen Gupta, D.K. Yadav, R. Gupta, M. Yadav, Highly dispersed MWCNTs coupled manganese salen nanostructure for simultaneous electrochemical sensing of vitamin B2 and B6, J. Electroanal. Chem. 807 (2017) 235–243.*

MWCNTs and an MWCNT-immobilized manganese salen composite [6]. The presence of manganese in the composite material indicates immobilized manganese salen [6]. Combined microscopic and EDAX mapping provides strong support for the characterization of CNTs and their composites.

AFM analysis provides additional support for the interpretation of surface morphology [77,78]. The roughness of the thin film of nanotubes in the form of the root mean square surface, mean surface, or average surface can be determined using AFM [77,78]. In addition, the tube diameter, height profile, particle size, and other physical properties can be interpreted using AFM analysis [75,79]. The AFM analysis of SWCNTs and an SWCNT-oxovanadium(IV) salen composite is shown in Fig. 5.9. The variation in roughness and the change in height profile indicate the presence of nickel salophen in the composite material [75].

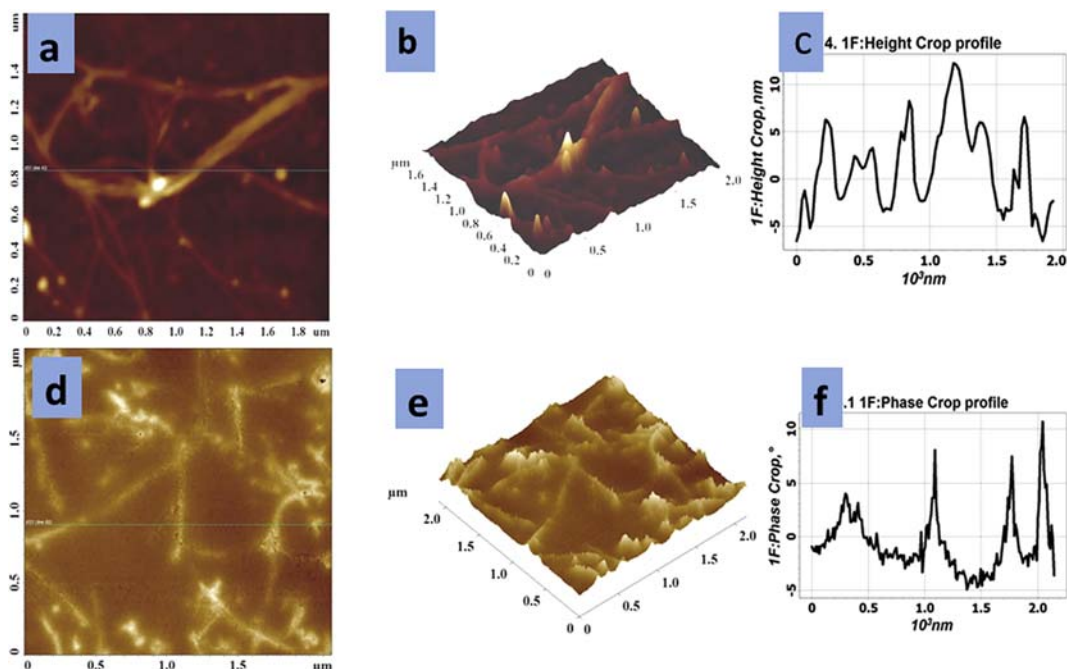


Figure 5.9

(A–C) Atomic force microscope images of single-walled carbon nanotubes (SWCNTs), (D–F) SWCNT-oxovanadium(IV) salen composite, and with corresponding (A, D) two-dimensional image, (B, E) three-dimensional image, and (C, F) section analysis, respectively. *Reproduced with permission from P.K. Sonkar, V. Ganesan, D.K. Yadav, R. Gupta, Dual electrocatalytic behavior of oxovanadium(IV) salen immobilized carbon materials towards cysteine oxidation and cysteine reduction: graphene versus single walled carbon nanotubes, ChemistrySelect, 1 (2016) 6726–6734.*

Without doubt, different microscopic techniques such as AFM, SEM, TEM, as well as EDAX and mapping provide strong characterization tools for the morphological study of CNTs. The characterization of CNTs and CNT-based composites with their microscopic details have been discussed: CNT-hybridized carbon fiber composites [80], polycarbonate CNTs composites [81], CNT–polymer composites [82], alumina-coated CNTs [83], hybrid materials with CNTs [84], polycarbonate with MWCNTs [85], well-dispersed SWCNTs polyaniline composites [86], MWCNT-manganese salen composites [6], and so on [9,87,88].

3.2 Raman spectroscopy

Raman spectroscopy is one of the most powerful tools for characterizing CNTs and their composite materials [89,90]. It is based on vibrational spectroscopy with numerous applications. It gives useful information regarding the electronic and phonon behavior of samples [3,89]. A low-energy photon as a probe is used in Raman spectroscopy. Because of this, it is a noninvasive and nondestructive technique. Raman spectroscopy provides a unique identity to CNTs because of the high optical response of the 1D nanotube

confinement of phonon and electronic states [3,89,90]. The Raman spectra of CNTs show the radial breathing mode (RBM) in the range of $100\text{--}500\text{ cm}^{-1}$ [3,91]. It is a unique phonon mode and arises only in the Raman spectra of CNTs. Thus, it is recognized as the fingerprint of the CNTs. The diameter of the CNTs shows an inverse relation with the RBM frequency. Hence, real-time monitoring of CNTs during its separation makes Raman spectroscopy more attractive. Defects in the nanotubes of CNTs can be recognized using the D-band, which appears at around 1300 cm^{-1} . The planar vibration of carbon present in the nanotube skeleton shows the G-band. The G-band appears for CNTs at around $1500\text{--}1600\text{ cm}^{-1}$ [3,92]. The G-band provides the difference between metallic and semiconducting SWCNTs. Two peaks of G-band appear in SWCNTs. The Lorentzian line shape G-band appears in semiconducting SWCNTs. However, a Breit–Wigner–Fano line shape G-band structure is observed in metallic SWCNTs [92]. A G' -band for CNTs appears at the Raman shift of $2450\text{--}2650\text{ cm}^{-1}$ based on the diameter and chirality of the CNTs. Raman spectra of the CNTs also show the M-band and iTOLA (second-order mode) [92]. These bands have less significance in the characterization of the CNTs. Raman spectra of SWCNTs and modified SWCNTs are shown in Fig. 5.10 [93].

Composite or functionalized CNTs can be identified using Raman spectroscopy by observing the change in D- and G-bands. For example, silver nanoparticles incorporated in CNTs show the change in Raman intensity compared with CNTs (Fig. 5.11A) [89]. The

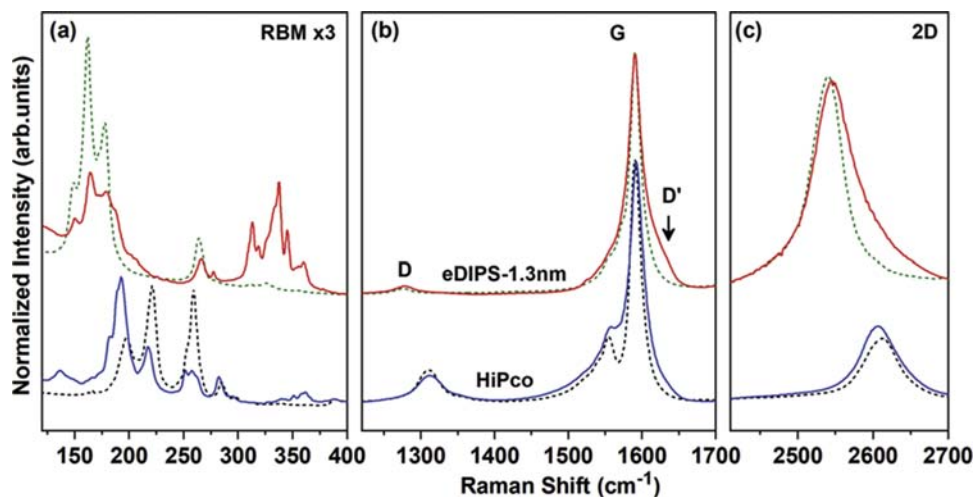


Figure 5.10

Raman spectra of pristine (*dashed lines*) and annealed (*solid lines*) enhanced direct injection pyrolytic synthesis with 1.3 nm-diameter (eDIPS-1.3 nm) (excited at 1064 nm) and high-pressure carbon monoxide (HiPco) single-walled carbon nanotubes (excited at 633 nm). (A) Radial breathing mode (RBM), (B) D- and G-bands, (C) Two-dimensional band. *Reproduced with permission from L. Shi, J. Wei, K. Yanagi, T. Saito, K. Cao, U. Kaiser, P. Ayala, T. Pichler, Templated direct growth of ultra-thin double-walled carbon nanotubes, Nanoscale 10 (2018) 21254–21261.*

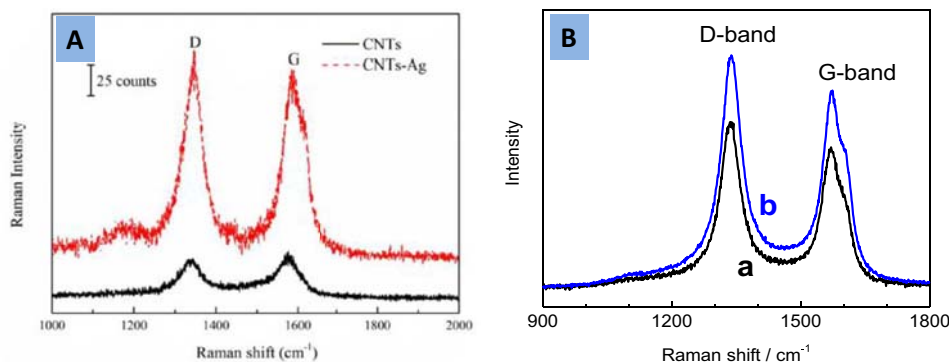


Figure 5.11

(A) Raman spectra of carbon nanotubes (CNTs) and silver nanoparticle–incorporated CNT composite. (B) Raman spectra of multiwalled carbon nanotube–manganese salen composite.

Reproduced with permission from P.K. Sonkar, V. Ganesan, S.K. Sen Gupta, D.K. Yadav, R. Gupta, M. Yadav, Highly dispersed multiwalled carbon nanotubes coupled manganese salen nanostructure for simultaneous electrochemical sensing of vitamin B2 and B6, J. Electroanal. Chem., 807 (2017) 235–243, X. Zhang, J. Zhang, J. Quan, N. Wang, Y. Zhu, Surface enhanced Raman scattering activities of carbon nanotubes decorated with silver nanoparticles, Analyst 141 (2016) 5527–5534, respectively.

Raman peak of D- and G-bands at 1343 and 1576 cm^{-1} , respectively, confirms the presence of CNTs. The change in Raman intensity of silver nanoparticle-incorporated CNTs increases about 21 and 26 counts for D- and G-bands, respectively [89]. This change in Raman intensity confirms the formation of composite material. Similar studies were observed in manganese salen-incorporated MWCNTs (Fig. 5.11B) [6]. It is clear from this discussion that a composite material can be identified using Raman spectroscopy.

4. Applications of carbon nanotubes and their composites

CNTs have a wide range of applications in various fields. They are significant for nanoelectronics, nanodevices, hydrogen storage, electrochemical sensors, biosensors, electrocatalysis, and more [12,13,15]. CNTs and their composite materials are useful in drug delivery, pharmaceuticals, and bio-nanomaterials [7,12]. They are useful for the lithium-ion batteries of computers, notebook, mobile phones, and other electronic appliances, which is the reason for the major commercial success of CNTs [14,94,95]. In addition, CNTs and their composites are used in fuel cells and solar cells as catalyst support, which reduces the cost of these cells [12,14,96,97]. CNTs are also used in water purification [98,99]. We have discussed the application of CNTs only briefly. For the detailed application of CNTs, readers are directed elsewhere [100–104].

5. Summary

CNTs are an important allotrope of carbon. The nanotubes of the CNTs are composed of sp^2 -hybridized carbon atoms. They are an attractive material owing to their significant properties, such as a high surface area, high tensile strength, stiffness, high thermal stability, and remarkable thermal conductivity. The functionalization or composite formation alters the physical properties of CNTs. The tensile strength and thermal stability can be enhanced by the formation of composite materials. Generally, epoxy groups provide more strength to CNT composite materials. A brief discussion was provided for the characterization of CNTs and their composite materials using SEM, TEM, AFM, EDAX, EDAX mapping, and Raman spectroscopy. These characterization tools provide the key to recognizing CNTs and their composite materials. For sure, CNTs and their composites are significant materials with a wide range of applications in almost every branch of science and technology.

Acknowledgments

University Grant Commission (UGC: M-14-58), India is gratefully acknowledged for financial support.

References

- [1] C.T. White, J.W. Mintmire, *Fundamental Properties of Single-Wall Carbon Nanotubes*, ACS Publications, 2005.
- [2] M.F. Yu, *Fundamental mechanical properties of carbon nanotubes: current understanding and the related experimental studies*, J. Eng. Mater. Technol. 126 (2004) 271–278.
- [3] R. Ghasempour, H. Narei, *CNT Basics and Characteristics*, Carbon Nanotube-Reinforced Polymers, Elsevier, 2018, pp. 1–24.
- [4] P.K. Sonkar, V. Ganesan, S.A. John, D.K. Yadav, R. Gupta, Non-enzymatic electrochemical sensing platform based on metal complex immobilized carbon nanotubes for glucose determination, RSC Adv. 6 (2016) 107094–107103.
- [5] R. Angadi, V. Koti, R. George, Carbon anotubes reinforced copper composites—a review, Int. J. Manuf. Eng. 3 (2016) 2393–8374.
- [6] P.K. Sonkar, V. Ganesan, S.K. Sen Gupta, D.K. Yadav, R. Gupta, M. Yadav, Highly dispersed multiwalled carbon nanotubes coupled manganese salen nanostructure for simultaneous electrochemical sensing of vitamin B₂ and B₆, J. Electroanal. Chem. 807 (2017) 235–243.
- [7] S.K. Prajapati, A. Malaiya, P. Kesharwani, D. Soni, A. Jain, Biomedical applications and toxicities of carbon nanotubes, Drug Chem. Toxicol. (2020) 1–16.
- [8] Q. Cao, Q. Yu, D.W. Connell, G. Yu, Titania/carbon nanotube composite (TiO₂/CNT) and its application for removal of organic pollutants, Clean Technol. Environ. 15 (2013) 871–880.
- [9] P.K. Sonkar, K. Prakash, M. Yadav, V. Ganesan, M. Sankar, R. Gupta, D.K. Yadav, Co(II)-porphyrin-decorated carbon nanotubes as catalysts for oxygen reduction reactions: an approach for fuel cell improvement, J. Mater. Chem. A 5 (2017) 6263–6276.
- [10] N. Yadav, M. Tyagi, S. Wadhwa, A. Mathur, J. Narang, Few biomedical applications of carbon nanotubes, Methods Enzymol. 630 (2020) 347. Nanoarchitectures built with carbon nanotubes and magnetic nanoparticles.
- [11] E.G. Rakov, The chemistry and application of carbon nanotubes, Russ. Chem. Rev. 70 (2001) 827–863.

- [12] P.M. Ajayan, O.Z. Zhou, Applications of Carbon Nanotubes, Carbon Nanotubes, Springer, 2001, pp. 391–425.
- [13] M. Endo, M.S. Strano, P.M. Ajayan, Potential Applications of Carbon Nanotubes, Carbon Nanotubes, Springer, 2007, pp. 13–62.
- [14] Y.H. Lee, K.H. An, S.C. Lim, W.S. Kim, H.J. Jeong, C.-H. Doh, S.-I. Moon, Applications of carbon nanotubes to energy storage devices, N. Diamond Front. Carbon Technol. 12 (2002) 209.
- [15] B.S. Sherigara, W. Kutner, F. D'Souza, Electrocatalytic properties and sensor applications of fullerenes and carbon nanotubes, Electroanalysis 15 (2003) 753–772.
- [16] S. Iijima, P. Ajayan, T. Ichihashi, Growth model for carbon nanotubes, Phys. Rev. Lett. 69 (1992) 3100.
- [17] Y. Ando, X. Zhao, T. Sugai, M. Kumar, Growing carbon nanotubes, Mater. Today Off. 7 (2004) 22–29.
- [18] M. Monthieux, V.L. Kuznetsov, Who should be given the credit for the discovery of carbon nanotubes? Carbon 44 (2006) 1621–1623.
- [19] S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, Nature 363 (1993) 603–605.
- [20] D. Bethune, C.H. Kiang, M. De Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls, Nature 363 (1993) 605–607.
- [21] J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam, R. Kizek, Methods for carbon nanotubes synthesis, J. Mater. Chem. 21 (2011) 15872–15884.
- [22] G.A. Rivas, M.D. Rubianes, M.C. Rodriguez, N.F. Ferreyra, G.L. Luque, M.L. Pedano, S.A. Miscoria, C. Parrado, Carbon nanotubes for electrochemical biosensing, Talanta 74 (2007) 291–307.
- [23] D. Qian, A. Wagner, J. Gregory, W.K. Liu, M.-F. Yu, R.S. Ruoff, Mechanics of carbon nanotubes, Appl. Mech. Rev. 55 (2002) 495–533.
- [24] H.G. Chae, T. Sreekumar, T. Uchida, S. Kumar, A comparison of reinforcement efficiency of various types of carbon nanotubes in polyacrylonitrile fiber, Polymer 46 (2005) 10925–10935.
- [25] R.H. Baughman, A.A. Zakhidov, W.A. De Heer, Carbon nanotubes—the route toward applications, Science 297 (2002) 787–792.
- [26] R.S. Ruoff, D. Qian, W.K. Liu, Mechanical properties of carbon nanotubes: theoretical predictions and experimental measurements, CR. Phys. 4 (2003) 993–1008.
- [27] J. Hone, M. Llaguno, M. Biercuk, A. Johnson, B. Batlogg, Z. Benes, J. Fischer, Thermal properties of carbon nanotubes and nanotube-based materials, Appl. Phys. A 74 (2002) 339–343.
- [28] M. Meyyappan, Carbon Nanotubes: Science and Applications, CRC Press, 2004.
- [29] N. Hamada, S.-I. Sawada, A. Oshiyama, New one-dimensional conductors: graphitic microtubules, Phys. Rev. Lett. 68 (1992) 1579.
- [30] M. Dresselhaus, G. Dresselhaus, A. Jorio, Unusual properties and structure of carbon nanotubes, Annu. Rev. Mater. Res. 34 (2004) 247–278.
- [31] X.L. Xie, Y.-W. Mai, X.-P. Zhou, Dispersion and alignment of carbon nanotubes in polymer matrix: a review, Mater. Sci. Eng. R. 49 (2005) 89–112.
- [32] P.C. Ma, N.A. Siddiqui, G. Marom, J.-K. Kim, Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review, Compos. A Appl. Sci. 41 (2010) 1345–1367.
- [33] E. Díaz, S. Ordóñez, A. Vega, Adsorption of volatile organic compounds onto carbon nanotubes, carbon nanofibers, and high-surface-area graphites, J. Colloid Interface Sci. 305 (2007) 7–16.
- [34] F. Gardea, D.C. Lagoudas, Characterization of electrical and thermal properties of carbon nanotube/epoxy composites, Compos. B Eng. 56 (2014) 611–620.
- [35] M.-F. Yu, B.S. Files, S. Arepalli, R.S. Ruoff, Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties, Phys. Rev. Lett. 84 (2000) 5552.
- [36] M.-F. Yu, O. Lourie, M.J. Dyer, K. Moloni, T.F. Kelly, R.S. Ruoff, Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load, Science 287 (2000) 637–640.
- [37] Z. Pan, S. Xie, L. Lu, B. Chang, L. Sun, W. Zhou, G. Wang, D. Zhang, Tensile tests of ropes of very long aligned multiwall carbon nanotubes, Appl. Phys. Lett. 74 (1999) 3152–3154.
- [38] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, Crystalline ropes of metallic carbon nanotubes, Science 273 (1996) 483–487.

- [39] R.S. Ruoff, D.C. Lorents, Mechanical and thermal properties of carbon nanotubes, *Carbon* 33 (1995) 925–930.
- [40] M. Samani, N. Khosravian, G. Chen, M. Shakerzadeh, D. Baillargeat, B.K. Tay, Thermal conductivity of individual multiwalled carbon nanotubes, *Int. J. Therm. Sci.* 62 (2012) 40–43.
- [41] X. Wang, Q. Jiang, W. Xu, W. Cai, Y. Inoue, Y. Zhu, Effect of carbon nanotube length on thermal, electrical and mechanical properties of CNT/bismaleimide composites, *Carbon* 53 (2013) 145–152.
- [42] F.C. Chiu, G.-F. Kao, Polyamide 46/multi-walled carbon nanotube nanocomposites with enhanced thermal, electrical, and mechanical properties, *Compos. A Appl. Sci.* 43 (2012) 208–218.
- [43] X. Jiang, Y. Bin, M. Matsuo, Electrical and mechanical properties of polyimide-carbon nanotubes composites fabricated by in situ polymerization, *Polymer* 46 (2005) 7418–7424.
- [44] S.M. Yuen, C.C.M. Ma, H.H. Wu, H.C. Kuan, W.J. Chen, S.H. Liao, C.W. Hsu, H.L. Wu, Preparation and thermal, electrical, and morphological properties of multiwalled carbon nanotube and epoxy composites, *J. Appl. Polym. Sci.* 103 (2007) 1272–1278.
- [45] T.E. Chang, A. Kisliuk, S. Rhodes, W. Brittain, A. Sokolov, Conductivity and mechanical properties of well-dispersed single-wall carbon nanotube/polystyrene composite, *Polymer* 47 (2006) 7740–7746.
- [46] X. Gao, L. Liu, Q. Guo, J. Shi, G. Zhai, Fabrication and mechanical/conductive properties of multi-walled carbon nanotube (MWNT) reinforced carbon matrix composites, *Mater. Lett.* 59 (2005) 3062–3065.
- [47] B. Dey, M.W. Ahmad, A. ALMezeni, G. Sarkhel, D.S. Bag, A. Choudhury, Enhancing electrical, mechanical, and thermal properties of polybenzimidazole by 3D carbon nanotube@ graphene oxide hybrid, *Compos. Commun.* 17 (2020) 87–96.
- [48] I. Tajzad, E. Ghasali, Production methods of CNT-reinforced Al matrix composites: a review, *J. Compos. Compd.* 2 (2020) 1–9.
- [49] T.Q. Tran, J.K.Y. Lee, A. Chinnappan, N.H. Loc, L.T. Tran, D. Ji, W. Jayathilaka, V.V. Kumar, S. Ramakrishna, High-performance carbon fiber/gold/copper composite wires for lightweight electrical cables, *J. Mater. Sci. Technol.* 42 (2020) 46–53.
- [50] T.Q. Tran, J.K.Y. Lee, A. Chinnappan, W. Jayathilaka, D. Ji, V.V. Kumar, S. Ramakrishna, Strong, lightweight, and highly conductive CNT/Au/Cu wires from sputtering and electroplating methods, *J. Mater. Sci. Technol.* 40 (2020) 99–106.
- [51] H. Haruna, M.E. Pekdemir, A. Tukur, M. Coşkun, Characterization, thermal and electrical properties of aminated PVC/oxidized MWCNT composites doped with nanographite, *J. Therm. Anal. Calorim.* (2020) 1–9.
- [52] J. Zhao, J.P. Lu, J. Han, C.-K. Yang, Noncovalent functionalization of carbon nanotubes by aromatic organic molecules, *Appl. Phys. Lett.* 82 (2003) 3746–3748.
- [53] J.Y. Yook, J. Jun, S. Kwak, Amino functionalization of carbon nanotube surfaces with NH₃ plasma treatment, *Appl. Surf. Sci.* 256 (2010) 6941–6944.
- [54] R.J. Chen, S. Bangsaruntip, K.A. Drouvalakis, N.W.S. Kam, M. Shim, Y. Li, W. Kim, P.J. Utz, H. Dai, Noncovalent functionalization of carbon nanotubes for highly specific electronic biosensors, *Proc. Natl. Acad. Sci. U.S.A.* 100 (2003) 4984–4989.
- [55] C.L. Ngo, Q.T. Le, T.T. Ngo, D.N. Nguyen, M.T. Vu, Surface modification and functionalization of carbon nanotube with some organic compounds, *Adv. Nat. Sci. Nanosci.* 4 (2013) 035017.
- [56] C.A. Dyke, J.M. Tour, Covalent functionalization of single-walled carbon nanotubes for materials applications, *J. Phys. Chem. A* 108 (2004) 11151–11159.
- [57] M. Baibarac, I. Baltog, C. Godon, S. Lefrant, O. Chauvet, Covalent functionalization of single-walled carbon nanotubes by aniline electrochemical polymerization, *Carbon* 42 (2004) 3143–3152.
- [58] A. Hirsch, O. Vostrowsky, Functionalization of Carbon Nanotubes, *Functional Molecular Nanostructures*, Springer, 2005, pp. 193–237.
- [59] H. Yu, Y. Jin, F. Peng, H. Wang, J. Yang, Kinetically controlled side-wall functionalization of carbon nanotubes by nitric acid oxidation, *J. Phys. Chem. C* 112 (2008) 6758–6763.

- [60] B. Singh, S. Lohan, P.S. Sandhu, A. Jain, S.K. Mehta, Functionalized carbon nanotubes and their promising applications in therapeutics and diagnostics, *Nanobiomater. Med. Imag.* (2016) 455–478. Elsevier.
- [61] A.F. Quintero-Jaime, D. Cazorla-Amorós, E. Morallón, Electrochemical functionalization of single wall carbon nanotubes with phosphorus and nitrogen species, *Electrochim. Acta* 340 (2020) 135935.
- [62] J. Saldaña, P. Gallay, S. Gutierrez, M. Eguílaz, G. Rivas, Multi-walled carbon nanotubes functionalized with bathocuproinedisulfonic acid: analytical applications for the quantification of Cu(II), *Anal. Bioanal. Chem.* (2020) 1–8.
- [63] V. Georgakilas, K. Kordatos, M. Prato, D.M. Guldi, M. Holzinger, A. Hirsch, Organic functionalization of carbon nanotubes, *J. Am. Chem. Soc.* 124 (2002) 760–761.
- [64] M. Holzinger, O. Vostrowsky, A. Hirsch, F. Hennrich, M. Kappes, R. Weiss, F. Jellen, Sidewall functionalization of carbon nanotubes, *Angew. Chem. Int. Ed.* 40 (2001) 4002–4005.
- [65] P.C. Ma, J.-K. Kim, B.Z. Tang, Functionalization of carbon nanotubes using a silane coupling agent, *Carbon* 44 (2006) 3232–3238.
- [66] Y. Wang, Z. Iqbal, S.V. Malhotra, Functionalization of carbon nanotubes with amines and enzymes, *Chem. Phys. Lett.* 402 (2005) 96–101.
- [67] S.B. Sinnott, Chemical functionalization of carbon nanotubes, *J. Nanosci. Nanotechnol.* 2 (2002) 113–123.
- [68] H. Kuzmany, A. Kukovecz, F. Simon, M. Holzweber, C. Kramberger, T. Pichler, Functionalization of carbon nanotubes, *Synth. Met.* 141 (2004) 113–122.
- [69] Y. Ying, R.K. Saini, F. Liang, A.K. Sadana, W. Billups, Functionalization of carbon nanotubes by free radicals, *Org. Lett.* 5 (2003) 1471–1473.
- [70] H. Peng, L.B. Alemany, J.L. Margrave, V.N. Khabashesku, Sidewall carboxylic acid functionalization of single-walled carbon nanotubes, *J. Am. Chem. Soc.* 125 (2003) 15174–15182.
- [71] W. Tu, J. Lei, H. Ju, Functionalization of carbon nanotubes with water insoluble porphyrin in ionic liquid: direct electrochemistry and highly sensitive amperometric biosensing for trichloroacetic acid, *Chem. Eur. J.* 15 (2009) 779–784.
- [72] A. Tonkikh, V. Tsebro, E. Obraztsova, K. Suenaga, H. Kataura, A. Nasibulin, E. Kauppinen, E. Obraztsova, Metallization of single-wall carbon nanotube thin films induced by gas phase iodination, *Carbon* 94 (2015) 768–774.
- [73] K. Kędzierski, K. Rytel, B. Barszcz, A. Gronostaj, Ł. Majchrzycki, D. Wróbel, Unusual conductivity temperature dependence of multiwalled carbon nanotube thin film, *Chem. Phys. Lett.* 712 (2018) 144–148.
- [74] S. Sweeney, S. Hu, P. Ruenaroengsak, S. Chen, A. Gow, S. Schwander, J.J. Zhang, K.F. Chung, M.P. Ryan, A.E. Porter, Carboxylation of multiwalled carbon nanotubes reduces their toxicity in primary human alveolar macrophages, *Environ. Sci. Nano* 3 (2016) 1340–1350.
- [75] P.K. Sonkar, V. Ganesan, D.K. Yadav, R. Gupta, Dual electrocatalytic behavior of oxovanadium(IV) salen immobilized carbon materials towards cysteine oxidation and cystine reduction: graphene versus single walled carbon nanotubes, *ChemistrySelect* 1 (2016) 6726–6734.
- [76] D. Chattopadhyay, I. Galeska, F. Papadimitrakopoulos, Complete elimination of metal catalysts from single wall carbon nanotubes, *Carbon* 40 (2002) 985–988.
- [77] M. Toader, H. Fiedler, S. Hermann, S.E. Schulz, T. Gessner, M. Hietschold, Conductive AFM for CNT characterization, *Nanoscale Res. Lett.* 8 (2013) 24.
- [78] N. Ferrer-Anglada, V. Gomis, Z. El-Hachemi, U.D. Weglikovska, M. Kaempgen, S. Roth, Carbon nanotube based composites for electronic applications: CNT-conducting polymers, CNT–Cu, *Phys. Status Solidi A* 203 (2006) 1082–1087.
- [79] L. Durrer, T. Helbling, C. Zenger, A. Jungen, C. Stampfer, C. Hierold, SWNT growth by CVD on Ferritin-based iron catalyst nanoparticles towards CNT sensors, *Sensor. Actuator. B* 132 (2008) 485–490.
- [80] F. An, C. Lu, Y. Li, J. Guo, X. Lu, H. Lu, S. He, Y. Yang, Preparation and characterization of carbon nanotube-hybridized carbon fiber to reinforce epoxy composite, *Mater. Des.* 33 (2012) 197–202.

- [81] L. Chen, X.J. Pang, M.Z. Qu, Q. Zhang, B. Wang, B.L. Zhang, Z.L. Yu, Fabrication and characterization of polycarbonate/carbon nanotubes composites, *Compos. A Appl. Sci.* 37 (2006) 1485–1489.
- [82] B.L. Wardle, D.S. Saito, E.J. Garcia, A.J. Hart, R.G. de Villoria, E.A. Verploegen, Fabrication and characterization of ultrahigh-volume-fraction aligned carbon nanotube–polymer composites, *Adv. Mater.* 20 (2008) 2707–2714.
- [83] V.K. Gupta, S. Agarwal, T.A. Saleh, Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal, *J. Hazard Mater.* 185 (2011) 17–23.
- [84] T. Seesaard, T. Kerdcharoen, C. Wongchoosuk, *Hybrid Materials with Carbon Nanotubes for Gas Sensing*, Semiconductor Gas Sensors, Elsevier, 2020, pp. 185–222.
- [85] P. Pötschke, A.R. Bhattacharyya, A. Janke, Melt mixing of polycarbonate with multiwalled carbon nanotubes: microscopic studies on the state of dispersion, *Eur. Polym. J.* 40 (2004) 137–148.
- [86] J.E. Huang, X.H. Li, J.-C. Xu, H.L. Li, Well-dispersed single-walled carbon nanotube/polyaniline composite films, *Carbon* 41 (2003) 2731–2736.
- [87] S. Wang, R. Liang, B. Wang, C. Zhang, Dispersion and thermal conductivity of carbon nanotube composites, *Carbon* 47 (2009) 53–57.
- [88] H.A. Shawk, S.R. Chae, S. Lin, M.R. Wiesner, Synthesis and characterization of a carbon nanotube/polymer nanocomposite membrane for water treatment, *Desalination* 272 (2011) 46–50.
- [89] X. Zhang, J. Zhang, J. Quan, N. Wang, Y. Zhu, Surface enhanced Raman scattering activities of carbon nanotubes decorated with silver nanoparticles, *Analyst* 141 (2016) 5527–5534.
- [90] M.S. Dresselhaus, P.C. Eklund, Phonons in carbon nanotubes, *Adv. Phys.* 49 (2000) 705–814.
- [91] M.S. Dresselhaus, A. Jorio, R. Saito, Characterizing graphene, graphite, and carbon nanotubes by Raman spectroscopy, *Annu. Rev. Condens. Matter. Phys.* 1 (2010) 89–108.
- [92] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman spectroscopy of carbon nanotubes, *Phys. Rep.* 409 (2005) 47–99.
- [93] L. Shi, J. Wei, K. Yanagi, T. Saito, K. Cao, U. Kaiser, P. Ayala, T. Pichler, Templated direct growth of ultra-thin double-walled carbon nanotubes, *Nanoscale* 10 (2018) 21254–21261.
- [94] C. de las Casas, W. Li, A review of application of carbon nanotubes for lithium ion battery anode material, *J. Power Sources* 208 (2012) 74–85.
- [95] X.M. Liu, Z. Huang, S. Oh, B. Zhang, P.C. Ma, M.M.F. Yuen, J.K. Kim, Carbon nanotube (CNT)-based composites as electrode material for rechargeable Li-ion batteries: a review, *Compos. Sci. Technol.* 72 (2012) 121–144.
- [96] Y.H. Liu, B. Yi, Z.G. Shao, D. Xing, H. Zhang, Carbon nanotubes reinforced nafion composite membrane for fuel cell applications, *Electrochem. Solid State Lett.* 9 (2006) A356.
- [97] S. Mukherjee, A. Bates, S.C. Lee, D.-H. Lee, S. Park, A review of the application of CNTs in PEM fuel cells, *Int. J. Green Energy* 12 (2015) 787–809.
- [98] S. Kar, R.C. Bindal, P.K. Tewari, Carbon nanotube membranes for desalination and water purification: challenges and opportunities, *Nano Today* 7 (2012) 385–389.
- [99] R. Das, M.E. Ali, S.B.A. Hamid, S. Ramakrishna, Z.Z. Chowdhury, Carbon nanotube membranes for water purification: a bright future in water desalination, *Desalination* 336 (2014) 97–109.
- [100] D. Lahiri, S. Ghosh, A. Agarwal, Carbon nanotube reinforced hydroxyapatite composite for orthopedic application: a review, *Mater. Sci. Eng. C* 32 (2012) 1727–1758.
- [101] S.R. Bakshi, D. Lahiri, A. Agarwal, Carbon nanotube reinforced metal matrix composites - a review, *Int. Mater. Rev.* 55 (2010) 41–64.
- [102] V.K.K. Upadhyayula, S. Deng, M.C. Mitchell, G.B. Smith, Application of carbon nanotube technology for removal of contaminants in drinking water: a review, *Sci. Total Environ.* 408 (2009) 1–13.
- [103] P. Zhai, J.A. Isaacs, M.J. Eckelman, Net energy benefits of carbon nanotube applications, *Appl. Energy* 173 (2016) 624–634.
- [104] N.K. Mehra, K. Jain, N.K. Jain, Pharmaceutical and biomedical applications of surface engineered carbon nanotubes, *Drug Discov. Today* 20 (2015) 750–759.