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3 Aerosol Synthesis of Single-Walled Carbon Nanotubes

Albert C. Nasibulin and Sergey D. Shandakov

3.1 Introduction

3.1.1 Carbon Nanotubes as Unique Aerosol Particles

Carbon nanotubes (CNTs) are a unique family of materials exhibiting diverse useful chemical and physical properties [1, 2]. The CNTs and especially single-walled carbon nanotubes (SWCNTs) were found to have exceptional mechanical, thermal, and electronic properties [1–3], which are strongly determined by their chiralities. A brief summary of the physical properties of SWCNTs and materials made of SWCNTs are collected in Table 3.1. SWCNTs are the strongest known material, with exceptionally high Young modulus of elasticity and tensile strength [4, 5]. Both thermal conductivity and electrical conductivity show remarkably high values. Nanotubes in a polymer matrix significantly improve the thermal and mechanical properties of the matrix material [6]. Taking into account the very high current density that the tubes can withstand without destruction, up to 10^7 A/cm², SWCNTs are believed to be an ideal material to replace copper and aluminum in integrated circuits. Semiconducting SWCNTs have electrical properties that are better than those of any known semiconductors. The hole mobility in SWCNTs is higher than in silicon metal oxide semiconductor field-effect transistors (FETs) and comparable to the in-plane mobility of graphene [7]. The applications of SWCNTs in microelectronics are not limited to the utilization of individual CNTs. Sub-monolayer random networks or aligned arrays of SWCNTs could behave as a thin-film semiconductor with a charge mobility of up to ~2500 cm^2/V·s [8]. An obvious advantage of CNT utilization in electronics is the possibility to create flexible and transparent components [8, 9]. Owing to their high specific surface area and developed microporous structure, CNT materials can be widely applied as filters, electrodes, effective adsorbents and absorbents, and so on [10].

CNTs have very interesting molecular structure. A SWCNT can be schematically created by rolling up into a cylinder a single graphene layer, which consists of carbon atoms packed in a honeycomb crystal lattice (Figure 3.1). Depending on
Table 3.1 Physical properties of individual SWCNTs and materials made of SWCNTs.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young modulus of elasticity</td>
<td>100–1470 GPa (compared to 200 GPa for high-strength steel)</td>
<td>[4]</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>30–200 GPa (compared to 1–2 GPa for high-strength steel)</td>
<td>[4, 5]</td>
</tr>
<tr>
<td>Thermal conductivity along the tube</td>
<td>~5600 W/m K (twice as high as that of diamond)</td>
<td>[5]</td>
</tr>
<tr>
<td>Electrical resistance of metallic CNTs</td>
<td>3 x 10^{-4} Ω cm at 300 K (compared to 2.82 x 10^{-6} Ω cm for Al and 1.72 x 10^{-6} Ω cm for Cu)</td>
<td>[12, 13]</td>
</tr>
<tr>
<td>Maximum current density (without destruction)</td>
<td>10^7 A/cm² at theoretical limit of 10^{13} A/cm² (compared to 10^7 A/cm² for copper wire of 1 mm diameter)</td>
<td>[14–16]</td>
</tr>
<tr>
<td>Hole and electron mobilities</td>
<td>(2–4) x 10^{6} cm^2/V s (compared to 450 and 1400 cm^2/V s for Si at 300 K)</td>
<td>[17, 18]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Materials made of SWCNTs</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Microporous structures</td>
<td>Porous diameter: ~0.7 to ~2 nm</td>
<td></td>
</tr>
<tr>
<td>Specific surface area</td>
<td>1800 m²/g for closed CNTs; &gt;2000 m²/g for open CNTs</td>
<td>[10]</td>
</tr>
<tr>
<td>Young modulus of composites</td>
<td>2.5 GPa for SWCNT—polyethylene composite (compared to 0.38 GPa for pure polymer)</td>
<td>[8]</td>
</tr>
<tr>
<td>Composite electrical resistance</td>
<td>10^4 Ω cm at 340 K (compared to 10^{13} Ω cm for pure polymer)</td>
<td>[19, 20]</td>
</tr>
<tr>
<td>Composite heat conductivity</td>
<td>10 W/m K (compared to 0.1–1 W/m K for pure polymer)</td>
<td>[19]</td>
</tr>
</tbody>
</table>

The method of rolling, one can get CNT structures with different helicities: achiral (zig-zag and armchair) or chiral (Figure 3.2). The zig-zag and armchair nanotubes correspond to chiral angles of 0° and 30°, respectively. There is a simple rule for the chiral indices (n, m), which allows the prediction of the electronic properties of SWCNTs: if the indices are equal (n = m), then the tube has armchair structure and possesses metallic properties; if (n – m)/3 gives an integer value, then the CNT is semimetallic; otherwise, it is semiconducting, with a bandgap of E_g = 0.9/D eV, where D is the tube diameter in nanometers [7].

The aerosol route is the most popular way to produce CNTs. All synthesis methods can be classified according to the carbon atomization as physical or chemical techniques. The physical method is associated with a high energy input to the carbon source (graphite or carbon black) by either arc discharge, laser, or induction heating evaporation [21–23]. For the synthesis of SWCNTs, a small amount of metal catalyst is usually required. Chemical production is based on the catalytic decomposition of carbon-containing precursors. An obvious advantage of this method is the possibility of producing CNTs at relatively low temperatures. The synthesis methods can be further divided into substrate-supported chemical vapor deposition (CVD) [24–26] and aerosol-supported (free-floating catalyst) CVD [27–30]. In the substrate-supported CVD process, the carbon precursor decomposes and CNT formation takes place on the surface of catalyst particles that are supported on a substrate. The substrates can be aerolized. In the free-floating catalyst or aerosol-supported CVD method, the whole process takes place in the gas phase or on the surface of catalyst particles suspended in the gas. As a catalyst, typically transition metals such as Fe, Co, or Ni are used.
3.1.2 History and Perspectives of CNT Synthesis

Intensive CNT research was initiated in 1991 by Sumio Iijima after his famous publication [31], in which he showed clear structures of double-walled and multi-walled CNTs. Single-walled CNTs were independently discovered by Iijima and Ichihashi [32] and Bethune et al. [21] in 1993. Nevertheless, investigations on CNTs (carbon filaments or fibers) had been performed for many years before the described events. The earliest paper that the authors could find, related to the synthesis and observation of tubular carbon structures with a diameter of around 100 nm, was published in 1946 by Watson and Kraftmann [33]. They examined caprene, the product of C9H12 polymerization over fine copper oxide catalyst below 300 °C. Caprene, the chemical formula of which can be represented as C6H6, was likely an intermediate product between the carbon precursor and CNTs. In 1952 Radushkevich and Lukyanovich published the first clear transmission electron microscope (TEM) images of 30–50 nm thick CNTs [34]. In 1960 Bacon investigated the growth, structure, and properties of coiled graphite whiskers grown by arc discharge [35]. In 1975 Baker et al. finished their series of studies with a description of the first mechanism of CNT growth, examining hydrocarbon decomposition over Pt–Fe particles [36]. Oberoi et al. produced hollow carbon fibers with a diameter below 10 nm (admittedly a single- or double-walled CNT) using an aerosol growth technique [37, 38]. The crystallographic relationship between catalyst (FeCo and FeNi) particles and grown carbon nanofibers was investigated in 1981 [39]. The same year, a group of Soviet scientists reported the results of TEM observations of the product of carbon monoxide (CO) disproportionation on an iron catalyst and suggested the first chirality model of CNTs [40]. In 1984 Tishbets attempted to answer the question “Why are carbon filaments tubular?” He considered the energy change during filament growth and explained the tubular structure formation as due to free-energy minimization [41]. Further investigations of the growth [42] and applications [43] of the CNTs and filaments proceeded intermittently until the boom of CNT research.

The widespread interest in CNTs was caused by their diverse useful properties, which provided various applications in many fields, such as emittance technologies, nanoelectronics, superstrong fibers, composite materials, catalysts, molecular wires, straws, gears, switches, and photonic materials, and so on. It is believed that many new applications for CNTs will be proposed in the very near future when this material can be supplied on an industrial scale. So far, the ordinary utilization of CNTs has been limited by their very high price [44]. Nowadays, the price for purified CNTs remains quite high for many bulk applications (40 USD/g from Kunming Guoli Nanotechnologies Co., China). In order to reduce the cost significantly and to provide satisfactory quantities, development of the available methods for CNT mass production is needed. The available techniques have been successfully utilized to synthesize these materials in laboratory-scale quantities, and only a few methods are able to manufacture SWCNTs in gram quantities.

The first success in producing substantial amounts of SWCNTs was achieved by Bethune et al. in 1999 by the arc discharge method [21]. They used graphitic carbon with a small amount of cobalt catalyst. Smalley’s group succeeded in growing high-quality SWCNTs at the 1–10 g scale by using laser ablation of a graphite target placed in an oven [13]. Later, the same group developed another method called the HiPco process [45], which will be discussed later. In 2000, the group led by D.E. Reasor from the University of Oklahoma developed the CoMoCat method utilizing Co- and Mo-impregnated fume silica particles in a CO atmosphere in a fluidized bed reactor [46], commercialized by SouthWest Nanotechnologies, Inc. One of the successful approaches for high-yield synthesis is based on the combustion of hydrocarbon–oxygen–catalyst precursors. This method has been extensively applied by different groups to synthesize SWCNTs [23, 47–50]. A Canadian group from the University of Sherbrooke has recently developed a large-scale system for the synthesis of SWCNTs using induction thermal plasma technology [21]. The method is based on the direct evaporation of carbon black and metallic catalyst mixtures in a radio-frequency plasma torch reaching extremely high temperature (~15 000 K). The 40 wt% purity SWCNT samples can be continuously synthesized at a production rate of 100 g/h.

Analyzing the various techniques for the synthesis of SWCNTs, we believe that aerosol-supported CVD methods have many advantages over other methods. Arc discharge and laser ablation methods rely on evaporation of carbon from solid carbon sources at temperature of 3000–4000 °C and therefore are very energy-consuming methods. Additionally, the nanotubes synthesized by carbon evaporation are in tangled forms, difficult to unbundle and purify. The CVD methods are operated at essentially low temperatures (about 600–1000 °C). From an industrial point of view, for many applications it is desirable to produce and/or directly deposit CNTs onto the required substrates, so that time-consuming steps of CNT purification from the catalyst and support, dispersion, and deposition processes are avoided. Therefore, the aerosol-supported CVD technique, which allows the production of high-quality clean SWCNTs, is more preferable. Supplementary advantages of the aerosol-supported method are the possibilities for on-line control of CNT quality and separate individual and bundled CNTs. The continuous CVD process is one of the most promising and powerful methods for high-yield synthesis under controlled conditions.

We have restricted this chapter by considering only SWCNTs produced by aerosol-supported CVD synthesis methods. Even though practically all synthesis techniques (except substrate-supported CVD) deal with aerosolized catalysts and CNTs, investigations of SWCNTs in the gas phase have widely been ignored. Practically all methods are limited to CNT synthesis and the characterization of the product. Evolution of CNT concentrations and aerosol particle diameters in the gas phase during growth have very rarely been discussed. The first reactors that allowed controlled aerosol-supported growth with subsequent investigations of CNTs as an aerosol object were built in 2002–2003 in the NanoMaterials Group (Helsinki University of Technology). In this chapter, two synthesis methods for controlled production of SWCNTs, that is, the hot-wire generator (HWG) [29] and the ferrocene-based method [30], will be described in detail.
3.2 Aerosol-Unsupported Chemical Vapor Deposition Methods

Many groups have successfully utilized the aerosol-unsupported CVD method for the laboratory-scale synthesis of SWCNTs. One of the most common ways to produce SWCNTs is based on the thermal decomposition of ferrocene (usually along with thiophene) dissolved in different carbon sources. A prototype of the reactor was built and used for the growth of carbon fibers in the 1980s by Endo [43]. An aerosol-unsupported continuous CVD method, in which SWCNTs are grown from a benzene–ferrocene–thiophene mixture at a temperature of 1200 °C, was developed in 1998 by Cheng et al. [51]. Rao and co-workers [52], and Bladh et al. [28] produced SWCNTs by pyrolyzing C2H2 and CH4, respectively, in the temperature range of 800–1200 °C. Iijima’s group at Japan’s National Institute of Advanced Industrial Science and Technology has been actively working on the growth of SWCNTs utilizing other different aromatic hydrocarbons [53].

Recently, a simple technique based on spray pyrolysis of ferrocene dissolved in alcohols has been reported [54]. A similar method has been utilized by a group led by A. Windle from Cambridge University for spinning fibers from single-, double-, and multi-walled CNTs [55]. Synthesis of macro-scale amounts of SWCNTs from a mixture of ferrocene–sulfur–acetylene was achieved by Xie Shihen and colleagues at the Institute of Physics (Chinese Academy of Sciences) [56].

For many purposes, the presence of impurities is the main concern limiting the application of SWCNTs. Usually, as-produced SWCNTs contain undesired by-products in the form of soot particles, amorphous carbon or unused catalyst. Purification of the CNTs is very expensive and sometimes as expensive as the production of the tubes. The amount of undesirable products can be decreased by proper selection of experimental conditions and precursors. In particular, non-graphitic carbon impurities can be avoided by utilizing CO as the carbon source, which is known to distillate only on the surface of catalyst. Here, three experimental techniques based on CO and utilizing different catalyst sources, that is, iron pentacarbonyl (HiPco process) [43], ferrocene [28], and supersaturated iron vapor in the HGW method [29] will be briefly described. In order to demonstrate aerosol methods for the synthesis of SWCNTs, on-line monitoring of the SWCNT products, gas-phase separation of the products, and studies of the SWCNT growth mechanism, only the ferrocene-based and HGW reactors will be considered.

3.2.1 The HiPco Process

The HiPco (high pressure CO) process was developed by Nikolaev et al. at Rice University in 1999 [57]. Nowadays, this method is well known as a technique to grow bulk quantities of SWCNTs. HiPco is based on CO disproportionation (Equation 3.1).

\[
2CO \rightleftharpoons CO_2 + C \quad \text{(3.1)}
\]

on the surface of iron particles. The catalyst is generated in situ by the thermal decomposition of iron pentacarbonyl (Fe(CO)5) in the reactor heated to 1000–1200 °C. The HiPco process occurs at high CO pressures (up to 50 bar), which significantly increases the CO disproportionation rate and thus enhances the SWCNT yield.

A schematic of the HiPco reactor is shown in Figure 3.3. A flow of cold Fe(CO)5 vapor containing CO is introduced into the reactor through a nozzle and turbulent mixed with a hot CO flow. The SWCNTs produced are collected by filtering the gas flow. The gaseous product, CO2, is removed by passing the flow through molecular sieves. The CO gas is purified, compressed, and introduced into the reactor. Recirculation is needed due to the very low CO conversion — typically the mole fraction of CO2 does not exceed 0.005% at the outlet of the reactor. The HiPco process allows the production of SWCNT material with a purity up to 97% at a rate of about 500 mg/h [58]. Recently, the HiPco process was applied to produce SWCNTs by thermal decomposition of ferrocene vapor without additional carbon sources [59].

3.2.2 Ferrocene-Based Method

The ferrocene-based method is also based on the catalytic CO disproportionation reaction (3.1). The main differences between this method and the HiPco process are the catalyst precursor source, the ambient pressure, and the laminar flow in the reactor. Utilization of ferrocene as a catalyst precursor allows high-quality SWCNTs to be produced in the temperature range of 600–1150 °C [30]. Ferrocene is vaporized at room temperature by passing CO (at a flow rate of 300 cm3/min) through a cartridge filled with ferrocene powder (Figure 3.4). The flow containing ferrocene vapor (0.8 Pa) is then introduced into the high-temperature zone of the ceramic tube (internal diameter 22 mm) reactor through a water-cooled probe and
mixed with an additional CO flow (100 cm³/min). The outlet of the water-cooled probe is at the wall temperature of around 700 °C, which is needed for fast heating of the vapor-gas mixture and the production of tiny catalyst particles. In order to enhance the yield, usually a small amount of water vapor (around 50 ppm) or CO₂ (around 600 ppm) is introduced into the reactor. The SWCNTs are collected either by filtering the flow for macroscopic investigations or by an electrostatic precipitator (ESP) for observation by transmission electron microscopy (TEM) or scanning electron microscopy (SEM). The distribution of aerosol CNT particles can be measured by a system comprising a differential mobility analyzer and a condensation particle counter. The gaseous composition of the products is measured by a Fourier-transform infrared (FTIR) spectroscopy system.

Raman measurements and TEM observations detected high-purity SWCNTs. As an example, Raman measurements carried out with 633 and 488 nm excitation wavelength lasers from a sample collected at 800 °C are shown in Figure 3.5. The existence of a radial breathing mode (RBM) in the low-frequency region (100–200 cm⁻¹) and the strong G-band (with peak at 1592 cm⁻¹) in the collected Raman spectrum indicate the formation of SWCNTs. A notable characteristic of the collected spectrum is a weak D-band (around 1300 cm⁻¹), indicating a low fraction of disordered carbon in the product. Depending on the experimental conditions, the diameters of the CNTs produced by this method can be varied from 1.1 to 2.0 nm.

![Figure 3.4](image1) Schematic representation of the ferrocene-based reactor.

![Figure 3.5](image2) Raman spectra of SWCNTs synthesized in the ferrocene-based reactor.

### 3.2.3 Hot-Wire Generator

The HWG method is an original method developed in the NanoMaterials Group (Helsinki University of Technology) for the growth of SWCNTs [29] and multi-walled CNTs [60]. This method is based on the introduction of pre-made catalyst particles into the reactor and mixing them with the carbon source. A ceramic tube, with 22 mm internal diameter, inserted inside a furnace, is used as the laminar flow reactor (Figure 3.6). The HWG, which is a resistively heated thin iron wire (0.25 mm diameter), was placed inside a ceramic tube with external and internal diameters of 13 and 9 mm inserted inside the reactor to maintain inert conditions for catalyst particle formation. The outlet of the HWG tube was placed at the location with a wall temperature of around 400 °C. The iron particles produced in the HWG tube were carried in a N₂/H₂ (or Ar/H₂) mixture with mole component ratio of 9/1 at a flow rate of 400 cm³/min and mixed with the outer 400 cm³/min CO flow. Inside the reactor, in addition to the Boudouard reaction (3.1), the following CO hydrogenation reaction occurs:

$$CO + H₂ \rightleftharpoons H₂O + C$$  \hspace{1cm} (3.2)

Downstream of the reactor, a porous tube dilutor (12 l/min) was used to decrease CNT bundling and to prevent product deposition on the walls by thermophoresis and diffusion. The reactor is operated at ambient pressure. The average residence time inside the reactor is about 2–3 s. In order to preserve the conditions for SWCNT formation, a small amount of etching agents, such as water vapor or carbon dioxide, can be added [61]. An important characteristic of this process is the efficiency of utilization of catalyst material. Practically all the catalyst particles initiate the growth of CNTs. The concentration of CNTs grown in the reactor
The DMA technique is widely used in the field of aerosol science for particle number size distribution (NSD) measurements and is based on the size classification of charged aerosol particles according to their electrical mobility in an electric field [64]. Particles with selected electrical mobility after the DMA are introduced to the condensation particle counter (CPC) for the concentration measurements. Scanning the voltage (typically applied to the internal electrode) enables the selected particle size to be changed within the range regulated by DMA sheath flow rate, voltage, and geometry.

Figure 3.7 shows an example of the NSDs of the product coming from the reactor under conditions in which the product consists of either inactive catalyst particles or bundles of SWCNTs. A clear difference in the NSDs can be seen in both ferrocene-based and HWG reactors. The total aerosol concentration drops about two to three times and the geometric mean diameter is shifted to larger sizes when the reactor parameters change from inactive to active conditions for SWCNT growth. This on-line technique significantly facilitates the execution of experimental work, especially when the parameters are tuned to find appropriate conditions for SWCNT growth. It is worth noting that the geometric mean diameters corresponding to the conditions of CNT growth in ferrocene and HWG reactors (100 and 35 nm, respectively) are determined by the geometry of the product (typically bundles) and do not give direct information about the length and diameter of the SWCNTs produced.

The description of the theoretical approach to the mobility of non-spherical particles in an electric field has been reported elsewhere [63]. The correlation between electrical mobility size measured with the DMA and physical size of high-aspect-ratio objects such as multiwalled CNTs and nanowires was considered in [65].

![Figure 3.6 Schematic representation of the HWG experimental setup.](image-url)

as well as the morphology of the products can be easily varied by changing the concentration or activation degree of the catalyst particles [60]. Depending on the experimental conditions, the diameter of the CNTs is determined by the catalyst particle size and varies from 1.1 to 1.4 nm [62].

### 3.3 Control and Optimization of Aerosol Synthesis

#### 3.3.1 On-Line Monitoring of CNT Synthesis

Despite progress in the synthesis of CNTs, their detection has typically been realized only by SEM, TEM, or spectroscopy methods (for example, Raman, photoluminescence or optical absorption). These techniques generally require additional work, they are time- and resource-consuming, and they do not give direct feedback to the synthesis process. In order to provide on-line information on the reactor process conditions, differential mobility analysis (DMA) technology was adapted [63].

![Figure 3.7 NSDs of the product formed in active and inactive CNT growth conditions in (a) the ferrocene-based reactor and (b) the HWG reactor using different carrier gases through the HWG tube.](image-url)
3.1.2 Individual CNTs and Bundle Separation

Ideally, even one SWCNT with a certain chirality placed in a certain location is sufficient for many applications, such as an FFT, memory device, quantum wire, or logic gate circuit. Therefore, methods for the controllable synthesis of individual CNTs are extremely desirable. However, this is still a challenging task, since CNTs tend to bundle spontaneously, and, as a result, most of the CNT synthesis methods produce bundled tubes. In order to exfoliate the bundles, additional steps of CNT functionalization, ultrasonication, and deposition are required. Isolated and individual CNTs can be synthesized by the substrate CVD method. Nevertheless, the requirement to use high growth temperatures (between 400 and 1000°C) inevitably limits the utilization of temperature-sensitive substrate materials and the simple integration of CNTs into nano-scale electronic devices.

A one-step process for the gas-phase CVD synthesis, in situ separation, and deposition of individual SWCNTs on a wide variety of substrates at ambient temperature has been developed. This approach is based on spontaneous charging of CNTs during their bundling in the gas phase [66, 67]. Charged CNTs were removed from the gas by passing them via an electrostatic filter (ESP). The remaining non-charged fraction was found to consist of individual CNTs, while the filtered charged fraction of the CNTs were bundled. The collection of the individual CNTs can be realized by thermophoresis or by utilizing a corona charger ESP. This opens new avenues for the direct integration of individual CNTs into molecular electronics based on both conventional oxidized silicon substrates and temperature-sensitive materials, for example, for flexible electronics.

3.3.3 CNT Property Control and Nanobud Production

Initial experimental investigations revealed unstable CNT production in the HWG and ferrocene-based reactors. Analysis of the experimental data showed that the difficulties were associated with the reactor wall conditions. It was found that, in order to provide stable CNT synthesis, the walls needed to be saturated by the catalyst material. Practically, this could be achieved either by deposition of the catalyst particles on the reactor walls or simply by using a reactor tube made of the catalyst material. Further investigations revealed the essential need for the presence of small amounts of etching agents (CO$_2$ or H$_2$O vapor) for the successful synthesis of CNTs [61, 68].

By varying the concentration of H$_2$O vapor or CO$_2$ introduced into the CNT reactor, SWCNTs covered with covalently attached fullerenes were synthesized. This material was termed carbon nanobuds, since the fullerenes on the surface of the SWCNTs were reminiscent of buds on a branch [69]. The introduction of H$_2$O and CO$_2$ into the ferrocene reactor revealed that the optimum reagent concentrations were between 45 and 245 ppm for H$_2$O (see Figure 3.8) and between 2000 and 6000 ppm for CO$_2$. Atomistic calculations based on density functional theory showed the possibility of the existence of fullerenes covalently bonded to the SWCNTs by [2+2] and [4+4] cycloaddition as well as the formation of one-body SWCNT-fullerene hybrid structures (Figure 3.9). Nanobuds possess...
advantageous properties compared to SWCNTs or fullerene alone, or in their non-bonded configurations. For instance, this structural arrangement of highly curved fullerenes and inert, but thermally and electrically conductive, CNTs was shown to exhibit enhanced cold electron field-emission properties [69]. Additionally, higher reactivity due to the presence of fullerenes opens new possibilities for the functionalization of SWCNTs. Furthermore, the attached fullerene molecules could be used as molecular anchors to prevent slipping of SWCNTs in composites. Owing to the charge transport between SWCNTs and functionalizing fullerenes, both the electrical and optical properties of the material can be tuned.

3.4 Carbon Nanotube Bundling and Growth Mechanisms

3.4.1 Bundle Charging

Commonly, for the DMA measurements, a radioactive bipolar charger is utilized for the artificial charging of the aerosol particles. It was observed that CNTs synthesized in both the ferrocene and HWG systems were naturally charged. Aerosol mobility size measurements were presented in two different ways: as distributions and as spectra. The mobility size distributions were measured by passing the aerosol-containing flow through a radioactive charger, and then a typical inversion procedure was performed to calculate the real aerosol concentration, assuming equilibrium charging in the charger [70]. Spectra in which the concentration of the naturally charged aerosol was not subjected to the inversion procedure were obtained without the charger. The mobility diameter, $D$, was calculated assuming a spherical shape and a single charge of aerosol particles on the basis of the Millikan equation [71].

Aerosol size distribution measurements of charged and non-charged CNTs showed that, depending on the concentration of CNTs in the HWG reactor, a certain fraction of the CNTs are charged. The higher the total concentration, the higher the fraction of charged CNTs [70]. The tubes produced in the ferrocene reactor were practically all charged due to higher CNT concentration. The fraction of charged CNTs was determined on the basis of DMA size mobility measurements using an $^{85}$Kr charger. Electrically neutral and all (neutral and charged) aerosol CNTs were measured after the ESF, where the potential was or was not, respectively, applied. The concentration of charged CNTs was detected to be 92% at 800 °C, 99% at 1000 °C, and 98% at 1150 °C. An example of the NSD and spectra obtained after the reactor at 1150 °C is shown in Figure 3.10. The CNTs were found to be charged both positively and negatively. At a temperature of 800 °C the concentration of negatively charged ions was about six times higher than that of positive CNTs. Increasing the reactor temperature to 1000 °C resulted in an increase of the fraction of positively charged CNTs: the difference decreased to a factor of 2. At 1150 °C, the spectra of both negative and positive polarities were very similar.

In order to detect the charging degree of the naturally charged CNTs, two different DMA in tandem were utilized in the aerosol experiments [72]. The results of the Gaussian function fittings for 80 nm mobility-selected CNTs showed that the CNTs possessed from one to five elementary charges (Figure 3.11), which indicated non-equilibrium charging of the CNTs.

In order to examine the nature of the ions that were emitted from the CNTs and thereby responsible for CNT ionization, laser desorption ionization time-of-flight (LDI-TOF) measurements of the CNT samples were carried out. Carbon-containing ions ($C_6H_4^+$, $C_7O_2H^+$, and $C_8O_2H^+$) were found to be responsible for the negative charging of the CNTs. The positive charging occurs because of electron emission. The bundle can become charged due to the emission

![Figure 3.10](image-url)  
**Figure 3.10** (a) Number size distributions of all and non-charged fraction of CNTs. (b) Mobility spectra of negatively and positively naturally charged CNTs. The measurements were carried out after formation in the ferrocene reactor operating at 1150 °C.

![Figure 3.11](image-url)  
**Figure 3.11** Results of tandem mobility measurements of naturally negatively charged mobility-selected CNTs at 80 nm. Charging states are represented as follows: original number of charges/number of charges after passing through the charger.
of electrons and ions by dissipation of the released van der Waals energy during CNT bundling. For instance, the bundling of two armchair (10,10) nanotubes leads to the total energy decrease as high as 0.95 eV/nm. Considering that the average length of our bundles is larger than 100 nm, bundling is expected to result in a very high energy release.

3.4 Growth Mechanism

The mechanism of CNT growth is usually investigated ex situ by studying the products prepared under different experimental conditions. Another approach to examine the mechanism of SWCNT formation, which can be easily realized in the aerosol technique, is to sample in situ from different locations in the reactor [68, 73]. These allow one to follow the changes in product morphology, state, chemical composition of catalyst particles, and length of the CNTs [73].

For in situ sampling, a stainless-steel rod with a TEM grid attached to the top was rapidly inserted into the reactor and held in a steady position for 30 s. The product was collected due to the thermophoretic forces between the hot reactor's atmosphere and the cold sampling rod. Aerosol product samples were taken from different positions inside the reactor. Multiple measurements made from TEM images determined the average length of the SWCNTs at different locations in the reactor. On the basis of the CNT lengths, temperature, and residence time in the reactor, the average growth rate of the SWCNTs was calculated. The calculations showed that the growth rate of the CNTs varied from 0.67 to 2.7 μm/s when the temperature changed from 804 to 915 °C. The activation energy was found to be Ea = 134 kJ/mol, which was close to the values reported in the literature for multi-walled CNTs, and could be attributed to the activation energy for the diffusion of carbon atoms in bulk solid iron with concentrations of carbon from 0.1 to 1 mass% [73].

Even though the catalyst particles are very small, the fact that they are in the solid state can be confirmed by calculations on the basis of the Kelvin equation:

\[
T_m = T_0 \exp \left( \frac{-2 \sigma V}{k \Delta H_m} \right)
\]

Here \(T_m\) is the melting temperature for a given particle of radius \(r\); \(T_0\) is the bulk melting temperature (1535 °C); \(\Delta H_m\) is the latent heat of fusion (13.8 kJ/mol); \(V\) is the volume of a metal atom, which can be calculated from the density (7.87 × 10^3 kg/m^3); and \(\sigma\) is the surface tension between the liquid and solid (0.86 J/m^2). As can be seen from Figure 3.12, the catalyst particles of around 4.5 nm in the temperature range of 804–915 °C should be in the solid state [73].

The shape of the catalyst particle determines the probability of the carbon atoms being on the surface. The particle shape is not always ideally spherical, and in addition to being convex can also contain concave regions, where the particle curvature is negative. In general, a system adopts a configuration that minimizes the surface energy. Owing to the diffusion process, the system continually changes and tends to occupy lower potential energy level. Therefore, the probability of carbon atoms being on the negative-curvature surface is higher since then carbon would get more neighbors compared to on convex regions. Therefore, excess carbon dissolved in a particle can preferentially segregate to regions with negative curvature. The existence of concave regions in the particles and the segregation conditions were observed during our TEM investigations and could be easily seen during in situ TEM studies of CNT growth [74, 75].

The results of the kinetic studies, which determined the limiting stage for CNT growth (carbon diffusion through the solid catalyst particle), TEM observations, and calculations allowed us to propose a mechanism for CNT nucleation and growth (Figure 3.13). The nucleation of CNTs is believed to occur from solid iron supersaturated by carbon. A concave region, where carbon segregation can occur preferentially, is created in the particle (Figure 3.13a). Carbon released on the surface forms a graphite cap (Figure 3.13b), a CNT nucleation site. The CNT starts to grow by feeding carbon into the concave regions, where the carbon atoms are consumed due to incorporation into the hexagonal CNT network. This leads to the creation of a carbon concentration gradient in the particle, which provides a continuous flux of carbon atoms through the catalyst particles from the surface to

![Figure 3.12](image)

**Figure 3.12** The effect of particle curvature on the melting temperature and carbon solubility in iron.

![Figure 3.13](image)

**Figure 3.13** Schematic representation of CNT nucleation and growth. (Courtesy of Anton Anisimov.)
the region of CNT growth. The concave region is preserved by the growing CNT, since the CNT walls are much stiffer than the iron particle. Part of the particle embedded inside the growing CNT in the initial stage (Figure 3.13c) is pulled out from inside of the CNT due to the surface tension of the catalyst particle (Figure 3.13d). Figure 3.13e corresponds to the conditions of steady-state growth of CNTs. It is worth mentioning that the proposed mechanism (Figure 3.13) is valid not only for SWCNTs, but also for the growth of multi-walled CNTs synthesized by the substrate CVD method [74, 75].

3.5 Integration of the Carbon Nanotubes

The main advantage of the considered aerosol methods is the possibility to directly integrate the CNTs into some applications without time-consuming sample purification, dispersion, and subsequent deposition. Since the CNTs are clean, they can be directly utilized in the form in which they come from the reactor. Since the CNTs are collected at room temperature, they can be deposited onto any substrate, including temperature-sensitive polymers. CNTs can be directly deposited onto the desired substrate by applying either thermophoretic or electrophoretic forces, or they can be simply filtered and subsequently transferred onto the secondary support.

Collection of CNTs from the gas phase can also be carried out using a thermophoretic precipitator. Thermophoresis is a physical phenomenon in which aerosol particles, subjected to a temperature gradient, move from high- to low-temperature zones [76]. A thermophoretic precipitator employs an electrically heated top plate (120 °C) and a water-cooled bottom plate (10 °C) with an aerosol sample flow through a gap between the plates [77]. Substrates for SWCNT collection are placed on the cold plate. Collection of both neutral and electrically charged CNTs from the gas phase onto substrates can also be carried out at ambient temperature using a point-to-plate ESP (Infotex Products, New Mexico, USA). In this device, CNTs are charged in a corona discharge that ionizes the gas and creates a small current between the two plates. Charged SWCNTs can also be collected on a substrate to which a certain potential is applied. This type of ESP is a cylindrical chamber with an inner horizontally positioned metal electrode, where the substrate is placed [78].

Deposited individual CNTs have been utilized to create high-efficiency FETs. Transistors made out of CNTs are known to have very high mobilities, but usually exhibit large hysteresis [79]. Nevertheless, the unwanted hysteresis in FETs could be successfully utilized in memory devices. Rinziki et al. [80] showed high-yield memory elements with an ON/OFF ratio up to 10^6 using a nanometer-thick gate dielectric deposited by atomic layer deposition.

Devices built on individual CNTs allow the study of the properties of tubes and are very important from the scientific point of view. However, they are resource- and time-consuming to manufacture and very difficult to manipulate. Usually, electron-beam and multiple-step nanolithography processes are required. However, for many applications, group properties of CNTs can be utilized. The uniformity of CNT properties is achieved by statistical averaging over a number of individual tubes comprising the network. This gives reproducible electrical behavior over larger length scales in comparison to individual CNTs, whose tube-to-tube variations in chirality, position, and orientation constitute a major fabrication obstacle [83]. Recently, a fabrication method for high-performance FETs based on SWCNTs deposited from an aerosol reactor was developed [83]. Two types of thin-film transistor structures have been fabricated to evaluate the FET performance of SWCNT films: bottom-gate transistors on Si/SiO_2 substrates, and top-gate transistors on polymer substrates. Devices exhibited ON/OFF ratios of up to 10^9 and field-effect mobilities of up to 4 cm^2/V s.

Filtering, which is the easiest way to gather aerosol particles from the gas phase, can also be utilized for some applications. Figure 3.14 shows the SWCNTs collected from a ferrocene reactor by filtering downstream of the reactor through 2.45 cm diameter nitrocellulose (or silver) disk filters (Millipore Corp., USA). Depending on the desired film thickness, the deposition time could be varied from a few seconds to several hours. A simple thermo-compression method for integrating SWCNT films of adjustable thickness, transparency, and conductivity into polymer films was proposed in [79]. Produced SWCNT-polyethylene composite films have exhibited good optical transparency and conductivity as well as high mechanical flexibility. It was found that the electrical conductivity of the SWCNT films could be significantly improved by ethanol densification. SWCNT-polyethylene thin films demonstrated excellent cold electron field-emission properties [79]. CNTs can also be transferred onto a mirror for laser mode locking [80] and onto a polystyrene terephthalate (PET) substrate for electrochemical applications [84] or for transparent and flexible electrodes for replacement of indium tin oxide (ITO) in flat displays. Various other devices and components based on CNT networks have already been successfully demonstrated, including diodes, logic circuit elements, solar cells, displays, and sensors.

![Figure 3.14 SWCNT film collected on nitrocellulose filters. (The numbers show the thickness value in nanometers.)](image-url)
3.6 Summary

In this chapter, research in the field of CNTs concerning their discovery, intriguing properties, and applications has been briefly reviewed. A comparison of different synthesis methods for both laboratory and industrial production was presented. Special attention was devoted to the aerosol-supported CVD method and its advantages in the controlled production and integration of CNTs. On-line monitoring of CNT fabrication using DMA measurements and separation of individual CNTs based on spontaneous charging of CNTs were considered. Direct integration of the CNTs produced by the aerosol methods into different applications, especially for high-performance flexible electronics, was briefly discussed.

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