Part One Overview of Synthesis, Characterization, and Applications in Biomedicine 1

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1.1 Introduction

1

The strength of carbon nanomaterials lies in the fact that most of their properties can be modified and adjusted, depending on the target application(s). The morphology, surface chemistry, as well as the physical properties of carbon nanomaterials are all susceptible to change by tuning the synthesis procedures, or by employing post-treatments. As the possibilities are almost unlimited, not only the materials scientists but also (bio-)chemists and biologists have at their disposal an immense playground to invent new materials for electronics, transportation, energy production and storage, or medicine. In the latter case, carbon nanomaterials – such as fullerenes, nanohorns, and nanotubes – have already contributed to the development of new biosensors, diagnostic tools, drugs, and therapies [1–4].

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Although nanomaterials such as fullerenes or carbon nanotubes (CNTs) are remarkably popular and already available from several suppliers—as in the case of any other chemical compound—their synthesis remains a dynamic field of research. Today, improvements are continuously being made to increase the selectivity of desired nanomaterialsas, as well as their purity and quality. In the case of CNTs, much progress has been made in controlling their diameter, length, and chirality—all of which may be critically important, depending on the desired application(s). In contrast to organic molecules, carbon nanomaterials do not exhibit a textbook structure; rather, they contain impurities, structural defects and heteroatoms, all of which may have possible implications for the target application. The aim of this chapter is to bridge the gap between materials scientists, biologists and/or biochemists, by showing not only how carbon nanomaterials are produced, but also highlighting the consequences that specific synthesis parameters have on the functionalization and application(s) of these materials in both biochemistry and biology.

1.2

General Concepts on the Synthesis of Carbon (Nano-)Materials

1.2.1

Uncatalyzed Synthesis of Carbon (Nano-)Materials

The uncatalyzed synthesis of carbon materials or nanomaterials always proceeds through the temperature-driven rearrangement of carbon atoms provided by a precursor. Precursors in any physical state—whether gaseous (carbon monoxide, hydro-carbons), liquid (thermoplastic polymers, hydrocarbons), or solid (wood, sugars, polymers)—can be employed [5]. Common examples are activated carbon produced from the pyrolysis of wood, or candle soot resulting from the incomplete combustion of wax. The thermal decomposition of the precursor proceeds through pyrolysis for gases, carbonization for liquids, and decomposition in the case of solids.

The structure of the resulting material depends on both the nature of the precursor and the temperature of treatment [5–8]. The variety of carbon materials which exists will not be discussed in more detail at this point, as most of these materials are not employed in the life sciences. However, a basic knowledge of the mechanisms involved during graphitization is important to better understand those parameters that are crucial during functionalization (see Sections 1.6 and 1.7). Carbon materials are composed of small crystallites – also termed basic structural units (BSUs) – that are crosslinked in either a three-dimensional (3-D) or a twodimensional (2-D) network [5, 8]. In the latter case, the material can be further graphitized. After synthesis, the crystallites (sp²-hybridized carbon) are interconnected with disorganized carbon, at which stage a large proportion of heteroelements is still present in the material (Figure 1.1).

Thermal treatment, performed in a vacuum or in an inert gas (annealing) at 1500 K, removes the heteroelements, while simultaneously any five-membered rings are converted into six-membered rings and the BSUs grow to form larger crystallites (Figure 1.1). At approximately 1900 K, the carbon atoms linking the BSUs become organized into large polycyclic molecules. However, the graphene sheets are not fully parallel (as in graphite), due to the existence of rows of sp³ carbon (defects). Finally, at 2500 K all of the carbon atoms become hybridized sp²,



Figure 1.1 Elementary steps occurring during the thermal treatment of graphitizable materials. The circles mark the presence of heteroatoms.

and are integrated into graphene sheets. The stacking is then considered to be perfect, such that synthetic graphite is obtained.

1.2.2 Catalyzed Synthesis of Carbon (Nano-)Materials

The decomposition of gaseous hydrocarbons on transition metals to form solid carbon deposits is a well-known phenomenon in heterogeneous catalysis. In petrochemistry, these reactions lead to coking of the catalyst and trigger its deactivation by encapsulating the active sites [9, 10]. Indeed, during the 1950s, several groups utilized such knowledge of catalyst deactivation to synthesize carbon filaments [11, 12]. Subsequently, during in the 1970s and 1980s, small vapor-grown carbon fibers (VGCFs) with diameters below 100 nm were synthesized via the decomposition of hydrocarbons on transition metal nanoparticles [13, 14]. As a consequence, the VGCFs were introduced into polymers for purposes of their reinforcement, or to render them electrically conductive (e.g., to dissipate electrostatic electricity in fuel pipes) [15]. Very soon, carbon fibers of different sizes were obtained by varying the catalyst or the reaction conditions. In 1991, Iijima described in his groundbreaking publication the structure of carbon nanotubes [16]. The subsequent enthusiasm for CNTs led many research groups to attribute their discovery to Iijima, although they were actually already observed in the 1950s [11, 12].

The mechanisms involved in the catalyzed synthesis of carbon materials differ radically from those associated with the pyrolysis of hydrocarbons. Typically, the hydrocarbons are decomposed to the elementary carbon atoms on the metallic surface of the catalyst, and then recombined to form solid carbon. Most carbon is directly incorporated into crystallites (sp² carbon) and the amount of sp³ carbon is significantly lower than for materials prepared by pyrolysis (Figure 1.2) [17, 18].



Figure 1.2 HRTEM images. (a) Soot particles; (b) Multi-wall carbon nanotube. Note that the crystallites are curved and shorter in the case of soot.

In addition, the morphology of the recombined carbon depends on the shape of the catalyst. For example, a planar surface will lead to graphene sheets, while a particle would produce carbon (nano-)fibers or single- and multi-wall CNTs (see Section 1.4). The catalyst, by definition, also acts on the kinetics of the solid carbon formation, by lowering the activation energy of the reaction. Consequently, the synthesis can also be conducted at a much lower temperature than the uncatalyzed pyrolysis, below 1200 K.

1.3

Synthesis from Solid Precursors

Carbon exhibits three natural allotropes for which all the atoms are in the same hybridization state: diamond (sp³ carbon); graphite (sp²); and carbyne (sp) [8, 19]. Starting from these allotropes, several polytypes (or families of carbon materials) can be distinguished which have carbon atoms of various hybridization states coexisting in the same material. For example, activated carbon and carbon black are made of crystallites (sp² carbon) interconnected with sp³ carbon atoms (see Section 1.2.1). At a very early stage, attempts were made to identify paths which linked the different polytypes and allotropes, there being a twofold aim to: (i) understand carbon materials formation in spatial dust; and (ii) be able to transform carbon materials on demand. In many of these fundamental experiments, solid carbon (usually graphite) was exposed to extreme conditions so as to dissociate and recombine carbon atoms and, indeed, several carbon nanomaterials were created, notably nanodiamonds, fullerenes, and CNTs.

1.3.1

Nanodiamonds

Nanodiamonds (NDs) constitute an emerging class of materials for biological, and in particular for medical, applications [20–24]. Although NDs have been known since the late 1950s [25], very few reports exist relating to their potential applications in the life sciences [21, 22]. Importantly, NDs have one major advantage over other carbon nanomaterials such as fullerenes and nanotubes, namely that their biocompatibility has already been demonstrated [22]. *Diamondoids*, which are subnanometer clusters of similar structure, are used in drugs [26]. For example, adamantane–the smallest of these clusters–is an important building block for drugs used to treat Parkinson's disease and Alzheimer's disease. Recently, a new synthetic technique has allowed the creation of ultrananocrystalline diamond (UNCD) films [27], which have been used to produce biosensors or to coat biomedical devices and implants. Unfortunately, this technique is incapable of producing NDs in sufficiently large amounts, and has therefore been restricted to niche applications [23].

Typically, ND nanoparticles exhibit sizes between 5 and 25 nm, and are therefore more suited than UNCD films to a broad range of applications in the life sciences,

for example as drug and gene carriers [21, 24]. Two different ND synthetic techniques which were developed during the 1960s are currently used on an industrial scale, namely shock-wave synthesis and explosive detonation. In both cases, high pressures and temperatures are generated in order to convert a solid carbon precursor into diamond.

1.3.1.1 Turning Graphite into Diamond

The high-pressure high-temperature (HPHT) synthesis, which was developed during the late 1950s [25], is based on the initial proposal of Rossini and Jessup (in 1938), and later by Bridgman, that there is a thermodynamic pressure and temperature equilibrium line between graphite and diamond in the phase diagram of carbon [28]. Therefore, it should be possible to directly transform graphite into diamond if the pressure and temperature are sufficiently high, and if the formed diamond can be quenched in order to avoid its retransformation into graphite. The research group at General Electric managed to circumvent the technical difficulties encountered, and developed an instrument that was capable of pressing graphite at up to 20 GPa and heating it at temperatures of up to 4000 K [29, 30]. In the early experiments, small diamonds were produced from a graphite bar at 13 GPa and 3300 K within a few milliseconds [29]. However, it was shown later that diamonds could also be produced under milder conditions if Group VIII transition metals were mixed with the graphite powder. The best results were obtained when using metal alloys, for example Ni-Fe-Mn, with diamonds being produced at 5 GPa and 1750 K [28]. As large amounts of metal or metal alloys were typically employed, interest was centered on the so-called "catalyst-solvent" effect, although because of the harsh synthesis conditions involved, studies of the growth mechanism with in situ techniques remained extremely challenging. To date, the role of neither the metal nor metal alloy has been fully elucidated, although several mechanisms have been proposed (see Refs [28, 31]). The HPHT technique is better suited to the synthesis of large diamonds (micron to millimeter scale), with diamonds of up to 2 carats (0.4g) currently being produced using this method [32].

During the 1960s, DuPont developed, in parallel, a procedure to recreate the HPHT conditions by using shock waves. For this, a steel plate is covered with explosive (e.g., trinitrotoluene; TNT) and placed in front of a physical mixture of iron and graphite. After detonation, the steel plate collides with the iron–graphite mixture at an approximate velocity of $5 \,\mathrm{km \, s^{-1}}$; this produces a peak pressure of 30 GPa and causes the temperature to increase to about 1000 K within a few milliseconds [32]. Shock-wave synthesis typically leads to high-quality, monocrystalline and polycrystalline particles (up to $60\,\mu\mathrm{m}$) that are then milled to obtain NDs of approximately 25 nm diameter [22].

1.3.1.2 Explosive Detonation Synthesis

Explosive detonation synthesis was developed during the 1960s in the former USSR [22, 23]. The process involves the creation of an explosion in a hermetic tank, with the explosive producing the HPHT conditions required to grow NDs, while simultaneously providing the necessary carbon atoms. An additional carbon

precursor is not needed. In this process, TNT or any other explosive is typically mixed with cyclotrimethylenetrinitramine (hexogen) in an oxygen-deficient ratio, after which the explosive is ignited in the closed tank which has previously been filled with an inert gas. Within a fraction of a second, the pressure in the tank can increase to 20-30 GPa, while the temperature may reach (locally) 3000 K. The excess carbon atoms in the gas phase are condensed into ND particles, typically of 5 nm diameter. Because of their extremely small size, NDs produced by detonation synthesis are often referred to as ultra-dispersed diamonds (UDDs) or ultrananocrystalline diamonds (UNCDs). In order to prevent the transformation of UNCDs into graphite, or their oxidation with CO, CO₂ and H₂O that has been generated by the explosion, the temperature must be rapidly lowered, at a rate of at least 3000 K min⁻¹. The result of the detonation is a mixture called "diamond soot"; this contains 40-80% diamonds, 35-45% graphite-like particles, and 1-5% metal and metal oxide impurities. The diamonds are then separated and purified by chemical treatment, with strong oxidants such as chromic acid [23] or gas-phase HNO₃ [33] being used to oxidize and dissolve the impurities. In general, depending on the purification procedure used, commercial samples contain 90-99% diamond and 1-10% graphite impurities.

Because of their size, UNCDs are perhaps more suited to biological applications than are NDs produced by shock-wave synthesis. However, it must be emphasized that UNCDs synthesized by detonation are composed of a diamond core covered by few shells of onion-like graphite, as well as a layer of disorganized carbon (Figure 1.3) [33, 34]. Aleksenskii *et al.* demonstrated that oxidizing treatments



Figure 1.3 Schematic representation of the UNCD structure. The diamond core (1) is covered with few onion-like graphite shells (2), as well as a thick disorganized layer containing curled graphene sheets (3), graphite-like nanoparticles (4), and metal oxide inclusions (5). Reproduced from Ref. [33].

under harsh conditions (e.g., with 70% HNO_3 in an autoclave at 523 K) is sufficient to remove the disorganized carbon layer, as well as most of the onion-like shells [33]. These oxidizing treatments also lead to the creation of many oxygen-containing functional groups on the UNCD surface. Both, the presence of onion-like graphite and/or of functional groups interfere during the synthesis of UNCD-based composites, as well as during biological applications [22] (see also Section 1.7).

1.3.2

Fullerenes, Nanohorns, Single- and Multi-Wall Carbon Nanotubes

Fullerenes were discovered in 1985, as a result of Kroto's experiments to understand the formation of carbon clusters [35]. For this, carbon atoms were evaporated from a graphite disk by laser ablation, and then allowed to condense and cluster in the cold part of the set-up. Kroto optimized the reaction conditions to obtain C₆₀ as a major product. It is interesting to note that theoreticians predicted the existence of fullerene (and even some of its properties) long before its discovery [19, 36]. Unfortunately, laser ablation produced only minute amounts of C₆₀. A second breakthrough occurred in 1990, when Krätschmer and Huffman developed a set-up to produce carbon clusters and soot, with the aim of identifying bands in the absorption spectra of interstellar dust [37]. The carbon atoms were evaporated by creating an electric arc (arc discharge synthesis) between two graphite electrodes in a chamber filled with 100-200Torr helium, such that carbon deposits containing soot and fullerenes were condensed on the cold parts of the chamber. This set-up allowed the gram-scale production of fullerenes, and permitted further study of their physical and chemical properties. Shortly thereafter it was found that, by introducing slight variations in the reaction conditions (e.g., using a DC current instead of AC, or different He pressures), both single- and multi-wall CNTs could be grown, using the same procedure [16, 38]. At a later date, single-wall carbon nanohorns were also obtained [39, 40].

Although fullerenes synthesized by arc discharge are typically mixed with other carbon materials, their purification is relatively easy. Fullerenes are soluble in various organic solvents [41], and so can be easily separated from other carbon materials such as soot by Soxhlet extraction (e.g., using toluene). Following evaporation of the solvent, a mixture of C_{60} with fullerenes of higher mass is obtained, and this can be further purified using liquid chromatography [19]. Alternatively, the fullerene/soot mixture can simply be filtered over a charcoal/silica gel plug, with a relatively high yield. However, in contrast to liquid-phase chromatography, this method might not be capable of separating C_{60} from small organic molecules, such as polycyclic aromatic hydrocarbons (PAHs) [19]. As PAHs are known to be both carcinogenic and mutagenic, it is important to take great care in the purification of C_{60} before their further use in biological applications. After purification, it is also important to consider possible reactions with oxygen when storing C_{60} in air. It has been shown that oxygen is adsorbed strongly onto the C_{60} surface and,



Figure 1.4 Molecular structure of the $C_{57}H_{33}N_3$ molecule during its cyclodehydrogenation on a platinum(111) surface to produce C_{60} . Adapted from Ref. [45].

depending on temperature, can form oxygen-containing functional groups such as peroxo species, which are also known to be cytotoxic [42, 43].

Although arc-discharge synthesis typically produces high-quality carbon nanomaterials, with very few structural defects, the method is difficult to scale up for mass production. Consequently, alternative synthesis techniques have been investigated and developed. In the case of fullerenes, wet chemistry [44], as well as the platinum-catalyzed cyclodehydrogenation of organic polyaromatic precursors offer interesting and scalable solutions (Figure 1.4) [45]. For CNTs, catalytic chemical vapor deposition (CCVD) offers the best results.

1.4 Catalytic Chemical Vapor Deposition

1.4.1 Definitions

Catalytic chemical vapor deposition (CCVD) is, as its name clearly indicates, a variation of the chemical vapor deposition (CVD) technique. Although the link seems obvious, many research groups have investigated CCVD via a purely catalytic approach, forgoing the knowledge acquired over more than 60 years with CVD. It is, however, essential to first grasp the fundamental physical and chemical phenomena that govern CVD in order to obtain a complete picture of CCVD. The rediscovery of CVD over the past few years has created new opportunities to synthesize single-wall carbon nanotubes (SWNTs) and multi-wall carbon nanotubes (MWNTs), without using a metal catalyst, and thus facilitating applications in both biology and medicine (see Section 1.4.5) [46–52].

The CVD of carbon was first employed during the 1880s, and has been widely developed since the 1950s [32, 53]. The process consists of the thermal decomposition (pyrolysis) of a gaseous carbon precursor (usually a hydrocarbon, such as methane, ethylene or acetylene) on the surface of a substrate (1.1):

$$C_x H_y \rightleftharpoons x C + \frac{\gamma}{2} H_2 \tag{1.1}$$

This reaction obeys thermodynamic and kinetic rules, which must be taken into account in order to obtain homogeneous carbon coatings. For hydrocarbon precursors, carbon deposition is thermodynamically favored at high temperature, above 1000 K. For example, CVD with methane as a precursor is performed at a temperature between 1373 and 1673 K [32]. Then, by adjusting the reaction parameters such as temperature, total pressure, gas velocity and nature, and the partial pressure of the carbon precursor, it is possible to control the deposition rate and quality of the carbon coating [54]. As the gas-phase pyrolysis of hydrocarbons leads to the formation of carbon blacks (soot-like particles), it is crucial that the reaction occurs on the surface of the substrate and not in the gas phase, in order to obtain homogeneous coatings.

For CCVD, a transition metal–generally Fe, Ni, Co or one of their alloys–is used to catalyze the decomposition of the carbon precursor. Consequently, the temperature of the reaction can be significantly decreased; typically, CCVD is carried out between 700 and 1273 K. Because the reaction is catalyzed, other carbon-containing precursors may also be employed; for example, carbon can be deposited by CO disproportionation [e.g., the Boudouard reaction; Eq. (1.2)]:

$$2CO \rightleftharpoons C + CO_2$$
 (1.2)

In contrast to hydrocarbons, the rate of the CO disproportionation reaction reaches a maximum at 900 K, after which CO_2 formation is thermodynamically favored and the reaction rate decreases [55, 56]. It must be emphasized that, as for CVD, the deposited carbon reproduces the shape of the metal substrate; that is, flat particles lead to flat graphene sheets, while round nanoparticles produce nanofilaments (nanotubes and nanofibers). The elementary steps involved in the formation of the nanofilaments are discussed in Section 1.4.2.

As no consensus has yet been reached, the scientific literature proposes confusing definitions for CNTs. The most common definitions derive from research groups who classify as a nanotube any carbon filament with an external diameter less than 100 nm and having a tubular shape – that is, with a cylindrical pore at its center. Unfortunately, however, a purely morphological definition does not take the structure of the nanofilament into account. Indeed, as can be seen in Figure 1.5, it implies that materials with a completely different structure, and thus with different physical and chemical properties, will share the same name [18]. In contrast, Dresselhaus and Endo defined a CNT as a nested coaxial array of SWNTs, with each nanotube being formed by a graphene sheet rolled into a cylinder of nanometer-size diameter [15]. In order to avoid any ambiguity in this chapter, and in the scientific literature in general, it is suggested that reference is made to Dresselhaus and Endo's definition, as this also meets the recent recommendations of the International Organization for Standardization (ISO) [57].

Some examples of carbon nanomaterials produced using CCVD are shown in Figure 1.5. Vapor-grown carbon (nano)fibers (VGCFs; also referred to as VGCNFs) are obtained by feeding methane and iron carbonyl (as catalyst precursor) into a horizontal reactor maintained at 1373K (Figure 1.5a). Typically, the VGCFs



Figure 1.5 HRTEM images highlighting the structural differences of (a) a VGCF, (b) a CNF, and (c) a MWNT. The inset in panel (a) shows a low-magnification TEM image of the same material (VGCF).

produced are significantly larger than the MWNTs, with 80–90 nm instead of 10–15 nm external diameter, and they also show a dual structure [18]. The core, which is grown catalytically, exhibits a fishbone-like stacking of the graphene sheets. However, because of the high temperature required for the reaction, a thick layer of pyrolytic carbon is also formed by CVD on the external walls of the VGCFs. The structures of commercial fishbone carbon nanofibers (CNFs) and MWNTs, obtained by CCVD of ethylene on Ni and FeCo nanoparticles, are shown in Figure 1.5b and c, respectively.

1.4.2 Mechanistic Aspects

The reaction mechanism involved in CCVD has been investigated since the 1970s, mainly as the result of research into heterogeneous catalyst deactivation. Indeed, the formation of carbon deposits represents a major issue for many important petrochemical processes [10]. In the case of the steam-reforming reaction, the hydrocarbons are converted to CO and H_2 . In this case, the reaction takes place under conditions where it competes thermodynamically with the Boudouard reaction (Eq. 1.2), or with the pyrolysis of the hydrocarbon [9]. Solid carbon, as a byproduct, can poison the catalyst by encapsulating the metal particles, leading to a complete deactivation of the catalyst support and lead to its fragmentation.



(a) Decomposition of the carbon-containing precursor on the surface of the catalyst particle; (b) Diffusion of carbon atoms through the particle as a solid solution; (c) Precipitation of carbon at the metal-support interface and formation of a nanofiber or a nanotube.

The first carbon filaments were observed, using electron microscopy, during the 1950s [11, 12, 19]. Some time later the pioneering studies of Baker on the formation of carbon filaments on nickel (a steam-reforming catalyst), as well as on Group VIII metals and metal alloys, led to the establishment of a growth mechanism which is still widely accepted today [58, 59]. In fact, Baker suggested that the vapor-liquid–solid (VLS) theory developed by Wagner and Ellis to explain the growth of Si whiskers [60] might be transposed to also explain the growth of carbon filaments [58]. The VLS mechanism consists of three successive steps (Figure 1.6) [58]. First, a carbon precursor present in the gas phase is adsorbed onto the surface of the catalyst particle, and then dissociates to form elementary carbon atoms. The carbon atoms then dissolve in the metal and diffuse though the particle. Finally, the carbon atoms precipitate at the metal–support interface to form a carbon nanofilament.

Whilst the VLS mechanism is still widely employed to explain the growth of CNFs, as well as of SWNTs and MWNTs [61–63], its validity is often discussed, with the main problem relating to the second step. Carbon diffusion on/through the catalyst particle would be expected to be the rate-limiting step of the reaction. Baker showed that the activation energy calculated from experimental data was in good agreement with values obtained for carbon dissolution in metal single crystals [58, 59, 64]. The results of recent kinetic experiments also support this mechanism in the case of CNFs and MWNTs grown on iron [63, 65, 66]. However the driving force which would push carbon atoms to diffuse through the whole particle remains unclear [67–72]. In addition, the VLS mechanism implies the formation of a metal carbide. Iron carbide (Fe₃C) is often observed using transmission electron microscopy (TEM) and X-ray diffraction (XRD) after growth. However fresh Fe₃C does not catalyze the CNT growth [73]. It appears, therefore, that iron carbide is either the deactivated catalyst, or is formed during cooling to room temperature.

Consequently, it was proposed by several groups during the late 1970s and 1980s that carbon diffusion should rather take place on the surface of the catalyst particle than through the particle [74, 75] and, indeed, many studies now support this hypothesis. More recent ab initio molecular dynamics simulations have shown that the surface diffusion of carbon atoms on a 1 nm Fe particle, and their incorporation into the forming graphene sheet, occurs significantly faster than does carbon diffusion in the bulk of the particle [76]. Raty et al. failed to observe any carbon atoms plunging into the surface of the metallic particle in their calculations, while Hofmann et al. demonstrated, both experimentally and theoretically, that the activation energy for surface diffusion is significantly lower than for bulk diffusion in the case of Ni, Fe, and Co [77]. Helveg et al. provided the first time-resolved in-situ TEM images of a MWNT growing from a Ni particle [78]. In this case, the lattice fringes of the Ni were observed throughout the experiment, thus proving that CNTs can grow from solid Ni particles. Hofmann et al. studied the chemical and physical state of nickel and iron particles extensively, using both in-situ TEM and in-situ X-ray photoelectron spectroscopy (XPS) [79-81]. It was concluded by these authors that CNTs grow from solid particles, and that a carbide formation could be excluded. Recently, Wirth et al. conducted an extensive reinvestigation of the reaction kinetics over a large range of temperatures and pressures [82], and showed the growth rate to depend both on dissociation of the hydrocarbon at the surface of the catalyst, and on surface diffusion of the atomic carbon. Thus, it appears that the diffusion of carbon through the particle, though plausible at high temperature (especially for iron), is in fact an exception [83-85]. Typically, CNTs probably grow following a three-step CCVD mechanism that involves dissociation of the carbon precursor, surface diffusion of the carbon atoms, and their precipitation in the form of a nanotube.

1.4.3

Single- and Multi-Wall Carbon Nanotubes

Both, SWNTs and MWNTs are typically synthesized with similar catalysts, with the diameter of the metal catalyst particle being the critical factor defining whether SWNTs or MWNTs are produced [86–92]. Large particles of 10 nm or more lead to MWNTs, whereas SWNTs are synthesized from particles smaller than 2 nm. In addition, the diameter of the CNT is most often directly proportional to the parent catalyst particle. Nasibulin *et al.* demonstrated that, for SWNTs, the particle is 1.6-fold larger than the corresponding nanotube, independent of the synthesis conditions [93]. In the case of SWNTs, it must also be highlighted that their electronic properties depend on their diameter, and on their chirality. A SWNT is formed by a graphene sheet rolled along an axis termed chiral vector C_h [13], which is defined by $C_h = n\bar{a}_1 + m\bar{a}_2$ (Figure 1.7), where a_1 and a_2 are the two vectors. In the (*n*,*m*) notation (*n*,0) and (0,*m*) denote zigzag nanotubes, whereas (*n*,*n*) are armchair SWNTs. All other (*n*,*m*) correspond to chiral nanotubes. A SWNT exhibits metallic properties when its |n - m| is a multiple of 3. In all other cases, the SWNT is semiconducting, and therefore, an armchair SWNT is always



Figure 1.7 Construction of a SWNT by rolling a graphene sheet along the chiral vector C_h . (a) Depending on (n,m), the SWNT can be zigzag, armchair or chiral; (b) Structure of a (5,0) zigzag SWNT; (c) Structure of a (6,0) armchair SWNT.

metallic. The number of (n,m) possibilities depends on the SWNT diameter (Figure 1.7). Control of the catalyst particle size is, therefore, of crucial importance.

1.4.3.1 Floating Catalyst CCVD

In the case of the floating catalyst CCVD technique, the catalyst precursor–usually a metallocene [94] or a metal carbonyl [56]–is directly vaporized in the reaction chamber at the same time as the carbon-containing precursors. The organometallic compound is immediately decomposed to form catalyst nanoparticles which remain suspended in the gas stream. In fact, two different reactions take place simultaneously: (i) the catalyst particle grows by CVD; and (ii) the SWNTs grow on the catalyst by CCVD, with the reaction conditions being very carefully controlled.

In the HiPCO process (developed at Rice University and based on this concept), iron carbonyl $Fe(CO)_5$ is injected along with carbon monoxide in a reactor maintained at 1300 K [56]. The iron particles are maintained at a diameter of 1–2 nm by utilizing a reverse CVD reaction (i.e., the reaction of Fe with CO to reform the volatile $Fe(CO)_5$), and in the meantime the SWNTs grow from the suspended Fe particles by CO disproportionation. In order to increase the CCVD reaction rate, the reaction is performed at 20 bar pressure. Compared to other processes, the HiPCO system produces high-quality SWNTs, with minimal carbon impurities (the main impurity is iron, but this can be removed with mild acid treatment). It has been shown recently that the floating catalyst CCVD also offers a degree of chirality control when tuning the composition of bimetallic catalyst nanoparticles,

thus opening a new route to the selective synthesis of semi-conducting or metallic SWNTs [94].

1.4.3.2 Immobilized Catalyst CCVD

Although floating catalyst CCVD offers excellent results, the complexity of the reaction and the relatively low yields typically obtained favor alternative processes. Of these, heterogeneous catalysts, where the active phase is immobilized on a substrate or in a matrix, represent the best option. Thus, by tuning the properties of the catalyst support as well as the catalyst synthesis parameters, it is possible to control the particle size and enhance the catalytic activity of the active phase.

During catalyst preparation, two steps have a major influence on the average particle size and its statistical distribution-namely, the catalyst synthesis, and its thermal pretreatment (e.g., calcination, reduction). A catalyst is usually composed of an active phase (the transition metal) as well as a substrate on which the active phase is deposited (the catalyst support), or a matrix in which the active phase is dispersed. A strong affinity between the metal and the support or matrix is important at each step of the catalyst preparation. In the case that the metalsubstrate interaction is low, the aggregation of metal atoms becomes easy, and large metal particles will be formed. Such aggregation can take place during impregnation of the support with the solution containing the metal salt precursor, during drying, during the calcination step (when the metal salt is decomposed into a metal oxide precursor), or during reduction (when the metal oxide is converted into the final metallic active phase). At the relatively high temperatures needed for calcination and/or reduction, the metal atoms and nanoparticles may become mobile and sinter to form larger particles. The latter are usually unselective in CNT synthesis, and typically become encapsulated with one or several layers of carbon. In addition, sintering may lead to a broader distribution of particle diameters. Subsequently, the final product may contain CNTs of various diameters, ranging from a few nanometers to more than 30 nm, and consequently aggregation and sintering must be avoided. In general, high-surface-area oxides, such as silica, alumina or magnesia, are employed as supports, as their strong interaction with the metal particles hinder their diffusion and sintering [95]. Several groups have shown that alumina provides the best results with most metals and metal alloys [96-98]. For example, Fe/Al₂O₃ and FeCo/Al₂O₃ are employed as catalysts in the industrial production of MWNTs [66, 99]. Mattevi et al. showed that, for Fe/Al₂O₃, Fe exists in 2+ and 3+ states at the interface with the support [98], and concluded that the Fe particles were chemically bonded to the alumina. This strong interaction led to smaller particles, with a narrower size distribution, than when Fe was supported on silica. In addition, the strain at the interface may well induce a reconstruction of the Fe particle, and this might account for the higher catalytic activity of Fe/Al₂O₃ compared to Fe/SiO₂. Another clear difference observed when replacing low-interaction supports (e.g., silica) with a high-interaction counterpart (e.g., alumina) lies in the change from a tipgrowth to a root-growth mechanism. The CNT growth mechanism (see Section 1.3.2) implies carbon precipitation at the rear of the particle, at the interface with

the support; as a result, the particle will be lifted and the growth catalyzed by the particle located at the tip of the nanotube (tip growth). However, if the metalsupport interaction is strong, the catalyst particle will remain anchored to the support surface, and growth will proceed with the particle located at the root of the CNT (root growth). Gohier et al. demonstrated that the mechanism could also switch from tip growth to root growth simply by decreasing the metal particle size [100], which explains why SWNTs usually follow the root growth mechanism. It should also be noted that, after reduction, the catalyst can be further modified by exposing it to defined gas compositions and temperatures. For instance, Zhou et al. showed that, under defined conditions, the metal particles would undergo a degree of structural reconstruction [101]; this allowed the growth of either platelet CNFs, fishbone CNFs or MWNTs, using the same catalyst, by simply varying the pretreatment conditions. The morphology (diameter, length), structure (alignment of the walls), existence of structural defects, homogeneity of the CNTs (same size), yield and formation of carbon-containing impurities are all parameters that depend on the growth conditions.

Alternatively, the metal can also be dispersed in mixed-oxide crystal structures, for example in perovskite type ABO₃ and spinel-type AB₂O₄ oxides [102]. The A or B crystallographic sites are then occupied by Fe, Ni, or Co cations. In this case, the metal remains typically dispersed in the oxide matrix during calcinations; however, during the reduction step the metal cations are reduced and metal nano-particles begin to nucleate. Zhao *et al.* showed that this technique would lead to the creation of homogeneous MWNTs [103].

1.4.4

Aligned Carbon Nanotubes

In general, CNT arrays are synthesized for applications in electronics (e.g., for field emission [4]), and therefore most studies have in the past focused on the growth of SWNT arrays on coated silicon wafers, although the techniques developed can also be used to grow MWNTs and/or CNFs. In addition, other supports can be employed, including either monolithic (plates) or in a powder form (alumina grains) [104]. Notably, the catalysts developed to synthesize randomly oriented CNTs can also be generally used to grow CNT arrays. For this, the Si wafers are first coated with a layer of silica or alumina, after which the metal is either deposited as a film by evaporation or by the CVD of ferrocene. A final thermal treatment with hydrogen or ammonia leads to dewetting of the support and the formation of metal nanoparticles [98]. The diameter of the nanoparticles-and consequently of the CNTs-is directly proportional to the thickness of the metal film. The critical parameter governing the growth of aligned CNTs is the density of the catalyst particles on the support. For example, if the density of the metal nanoparticles is low, then the SWNTs will grow in random directions [98]. The density of the SWNTs must reach approximately 5×10^{11} per cm² in order to become vertically aligned [105]. In this situation, the neighboring SWNTs will then support each other in a concerted step, and growth will proceed as a

"forest," orthogonal to the support. Parameters such as the temperature, pressure, and nature of the precursor each have a major influence on the quality of the mat, and on the length of the nanotubes [82]. In general, plasma-enhanced CVD (PECVD) provides better results because the plasma dissociates the hydrocarbon precursor to more reactive species. By using PECVD, Hofmann et al. were able to grow aligned nanofilaments at 393 K, which made it possible to synthesize forests on thermally unstable films such as plastics. However, it was noted that below 543 K, the structure of the nanofilament was essentially amorphous because insufficient energy was given to the system to anneal any defects [106]. Reasonably organized CNFs were obtained at temperatures in excess of 663 K. In order to increase the life time of the catalyst, oxidizing compounds such as water were added to the feed, in order to prevent any coke formation that could poison the catalyst. This "super-growth" technique led to very long SWNTs [107], with arrays of more than 0.5 mm being obtained within a few minutes [108]. Because of the high density of SWNTs, the growth rate can decrease due to diffusion limitations of the reactant gas molecules to the metal nanoparticles (root growth). However, this problem can be circumvented by patterning the catalyst so that CNT-free channels exist where the gas molecules can diffuse freely [109]. It was also shown that the geometry of the reactor would play a significant role. Typically, a cold wall shower head reactor offers the best results, because the reactants are fed directly orthogonal to the catalyst [110].

1.4.5

Carbon Nanotubes Synthesized from Biocompatible Catalysts

Although Fe, Ni and Co are the best catalysts to grow CNTs, it has been shown that many other elements can be used to grow CNTs [111]. Recently, several groups have demonstrated the possibility of growing SWNTs on oxides, such as silica [49, 50], alumina [49], or zirconia [52]. The nucleation and growth of the SWNTs was either attributed to CVD on solid silica nanoparticles [50] or at a molten silica particle of diameter <2 nm [49]. It was also suggested that the SiO₂ particles were first transformed into SiC by a carbothermal reaction, and that the SiC particles then catalyze the CVD [48]. In any case, this observation constitutes a break-through in CNT synthesis. Both, SWNTs and SWNT arrays can be grown on virtually any support, the only limiting factor being the formation of nanoparticles. In these preliminary studies, silica nanoparticles were formed either by the sputtering of SiO₂ (instead of thermal growth under oxidative conditions) [50] or by scratching the surface with a Si wafer [50] or a diamond blade [49].

Liu *et al.* showed that it is possible to grow short SWNTs on these transition metal-free supports [51], because the growth velocity was significantly lower $(8 \text{ nm s}^{-1} \text{ instead of } 4-20 \,\mu\text{m s}^{-1}$ for metal catalysts). Consequently, Liu *et al.* were able to control accurately the length of the SWNTs–a technique which in future might be of great interest for biological applications. The fact that CNTs are shorter and do not contain any metal impurities would favor their phagocytosis and reduce their pathogenicity [112].

1.4.6 Metal- and PAH-Induced Toxicity of Carbon Nanotubes

Since the evaluation of CNT-related toxicity is a time-demanding process, most investigations are ongoing. In the past, preliminary results have often been contradictory depending on the CNT products, their purification, and their functionalization. However, there appears to be some level of agreement with regards to the cytotoxicity of the remaining catalyst particles. In 2007, Pisanic et al. showed that iron oxide nanoparticles hindered the growth of neurons [113]. Both, SWNT and MWNT products contain various amounts of transition metals as well as oxide impurities from the catalyst supports. Depending on the synthesis process used and their possible purification, CNTs contain between 1% and 30% of inorganic impurities [114, 115], most of which can be easily removed by washing with acids and bases (see Section 1.5). The presence of carbon impurities is usually neglected, except in the case of SWNTs prepared by arc discharge, which can contain up to 30-50% carbon soots in the raw material [19]. Commercially available CCVDprepared SWNTs and MWNTs are expected to be free of carbon impurities-an assumption which is generally based on images recorded using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). At very high magnification, however, the CNT's surface is rarely clean (see Figure 1.8), with large amounts of carbonaceous debris being observed. Such debris includes large polycyclic molecules (most likely graphene sheets fragments) formed during the CNT synthesis. Although PAHs exhibit a similar structure, they are significantly



Figure 1.8 HRTEM image of a commercial MWNT. Most MWNTs exhibit various amounts of carbonaceous debris dispersed on their surface. In some cases, the debris can almost completely cover the nanotube's surface (arrows in the image).

smaller, and therefore it is very difficult to observe them even when using highresolution TEM (HRTEM). The PAHs are known to be carcinogenic and mutagenic and, if present on the CNT surface, they may have a significant influence on the results of toxicity studies. Plata et al. investigated the PAHs present in different CNT products and also in the gas stream during CNT synthesis [116, 117], and in both cases concluded that whilst some PAHs were observed, their concentrations were lower than were found in the air. Nonetheless, these results must be regarded with great caution. In the case of PAHs present in the gas phase, only the CCVD reaction performed with ethylene as carbon precursor was investigated. Although the reaction conditions are relevant to industrial CNT production, higher PAH concentrations may be identified for bench-scale CNT synthesis when other precursors are employed. When PAHs were present in commercial CNT products, Plata et al. used organic solvents to extract them. Although extraction with toluene is an effective and well-known purification technique for fullerenes, it has not been shown as successful for extracting PAHs from CNTs, as the PAHs interact strongly with the CNT walls via van der Waals interactions. Consequently, noncovalent functionalization techniques have been developed, in which desired functions are grafted onto pyrenes (see Section 1.7). Subsequently, the interaction between the arene and the CNT was shown to be strong, with the functional groups anchored irreversibly onto the CNTs walls, such that a total extraction of the PAHs would not be possible. Finally, the high affinity of PAHs for CNTs was confirmed by Yang et al., who suggested that, with time, PAHs present in the air might be adsorbed onto CNTs, thus increasing their potential toxicity [118].

1.5

Purification Techniques

The purification of CNTs involves the removal of any inorganic impurities as well as disordered carbon present in the raw product. Inorganic impurities mainly consist of the remaining catalyst, although additional impurities derived either from the catalyst preparation or from the CNT synthesis and handling may be identified. Although, in general, Fe, Ni or Co, as well as alumina, silica and magnesia, are found (Figure 1.9) [114, 115], Cr, Cu, Mo or Mn have also been found occasionally in the raw material. Washing with mineral acids such as HCl, HNO3 and H₂SO₄ represents a cheap and efficient method to remove most of the inorganic impurities. On some occasions, the acid treatment is followed by a base treatment, which is more efficient for dissolving the catalyst support. To date, the reaction conditions reported have varied widely with regards to the concentration of acid, and the reaction temperature and reaction time. Typically, the acid washing is conducted with concentrated HNO₃, at between 373 and 403 K, and for 2 to 20 h. Nitric acid is used most often because it is a strong acid and also a good oxidant; this allows any metal impurities to be dissolved and most of the disordered carbon to be oxidized in a single step. Unfortunately, this method has one major disadvantage, in that its efficiency varies for different CNT products, and so the condi-



Figure 1.9 SEM images of commercial CNTs obtained from (a) secondary electrons and (b) back-scattered electrons. The back-scattered electron signal is a function of the atomic number of the elements in the sample. Remaining catalyst particles appear as bright spots in the image, making their detection easier (arrows).

tions must be optimized. Whilst weak conditions might not be effective for removing all of the impurities, a strong treatment would functionalize the CNT surface and create a wide variety of oxygen-containing functional groups [119]. In the worst case, the CNT might even be destroyed. Notably, SWNTs are more reactive than MWNTs because of their curvature, and are easily damaged under strong oxidizing conditions. Salzmann et al. have developed a simple technique to remove most of the carbonaceous debris covering SWNTs, without destroying them [120, 121]. Initially, the debris and the SWNT surface are oxidized with HNO₃, after which the oxidized SWNTs are washed with sodium hydroxide solution. Because of the high pH, the surface acidic groups will be deprotonated, while both the debris and the CNTs will become negatively charged. The consecutive electrostatic repulsion is sufficiently strong to detach the debris from the CNT surface, and it can be removed by washing with distilled water, followed by simple filtration and rinsing. After purification, the CNTs can be annealed at high temperature in vacuum or in inert gas, in order to remove the functional groups and heal any defects.

Recently, much effort has been expended in developing new catalysts capable of growing SWNTs with desired chiralities. This task is extremely challenging, and, instead several research groups have developed parallel techniques to separate metallic from semiconducting SWNTs. Details of the various procedures employed, as well as their advantages and drawbacks, have been reported [105]. Arnold et al. have shown that it is possible to separate not only metallic from semiconducting SWNTs, but also SWNTs of different sizes, by using density-gradient

ultracentrifugation. This technique is nondestructive and, to date, has provided the best results [122].

1.6

Importance of Defects and Curvature for Further Functionalization

The reactivity of CNTs upon further functionalization with heteroatoms as well as with organic and organometallic molecules is not clear. Most of the exposed CNT surface area is constituted by the basal plane of graphite, which is known to be poorly reactive. All of the carbon atoms are hybridized sp², and the π electrons are delocalized over the entire nanotubes; this not only increases the stability of the structure but also provides the reason why CNTs are chemically stable in most aggressive media. In contrast, nanodiamonds are composed only of sp³ carbon atoms, with their surface being terminated by C-H bonds; consequently, hydrogen can be replaced relatively easily with desired functional groups or molecules [22]. Fortunately, however, the CNT surface is not perfect and flat (as in graphite), and a variety of topological defects exist as well as vacancies (Figure 1.10a) [123]. During their synthesis, heteroatoms such as nitrogen or boron can also be inserted into the backbone of the CNT, and it is possible to take advantage of these structural defects to anchor the desired molecules. Very often, CNTs are first oxidized with HNO3 in order to create a variety of oxygen-containing groups on their surface; these groups may then be employed as anchoring points to graft the desired molecules [115, 124-128]. Recently, Tessonnier et al. developed a concept based on the defect-mediated functionalization of MWNTs [129]. In this case, carbon atoms located close to vacancies are terminated with hydrogen, in order to replace the missing carbon atom. These potentially reactive C-H bonds may be regarded as possible anchoring points for the direct grafting of desired groups or molecules by C-C coupling reactions.

In the case of SWNTs, the small diameter induces a strong curvature (as occurs with fullerenes). Subsequently, the strain caused by the curvature leads to a pyramidalization of carbon atoms [126], such that the sp² hybridized orbitals are no longer in the same plane, but rather form an angle of 11.6°, which is very close to the angle expected for sp^3 carbon atoms. It is, therefore, not surprising that C_{60} is very reactive towards addition reactions, where sp² carbon atoms become sp³. Nyogi *et al.* calculated the pyramidalization angle as well as the π orbital misalignment angle as a function of the SWNT diameter and chirality (Figure 1.10b) [126]. These authors showed that, for small SWNTs, the pyramidalization angle is close enough to the value obtained for C₆₀ to expect a similar chemistry. Whilst SWNTs are certainly less reactive than C60, cycloaddition reactions would be expected to take place. In contrast, the curvature of the MWNT basal plane and the corresponding strain are too low to expect a similar chemistry to occur. Cycloaddition reactions might take place on a Stone-Wales defect, as their local curvature is similar to that of C₆₀. However, grafting directly onto a defect-free sidewall remains a major challenge, and defects would be required in this case.



Figure 1.10 (a) HRTEM image of a MWNT showing the presence of topological defects as well as vacancies; (b) Pyramidalization angle and misalignment of π orbitals in a (5,5) SWNT. Reproduced from Ref. [124].

1.7 Functionalization: Creating Anchoring Points for Bioactive Molecules

A broad variety of functionalization techniques has been developed for the further application of carbon nanomaterials in materials science as well as in the life sciences [115, 124–128]. Attention will be focused here on procedures developed to

functionalize CNTs, bearing in mind that similar techniques can be employed for nanodiamonds and fullerenes. Functionalization is an important step, as it allows CNTs to be opened, to be dispersed in solutions, to graft desired functions onto their surface, or for them to be coupled with another material. It is possible to distinguish three different families of functionalization techniques, namely oxidations, organic chemistry coupling reactions, and noncovalent functionalizations.

1.7.1

Functionalization by Oxidation

The oxidation reactions are the most popular because they permit the simultaneous purification of CNTs, the opening of their caps, and the functionalization of their surfaces. Various oxidants are employed, including HNO₃, H₂SO₄, H₂O₂, aqua regia (HCl:HNO₃, 3:1), KMnO₄, O₂, O₃, and H₂O. Of these oxidants, HNO₃ is certainly the most widely employed, because the treatment is relatively simple, efficient, and less dangerous than when using other oxidants. In addition, HNO₃ is expected to mainly create carboxylic acid groups, on which desired molecules can later be grafted by amidation or esterification. Although this belief is still widespread, especially in the life sciences, it has been shown that oxidizing treatments-and especially HNO₃ treatments-are unselective. Typically, a variety of oxygen-containing groups is created simultaneously (Figure 1.11a), all of which show different acidic and even basic properties. All of these groups must be taken into account when predicting the dispersion of CNTs in solutions, and the properties of the synthesized material. For example, it has been shown that NR₂-MWNTs synthesized with oxidized MWNTs are significantly less basic than when untreated MWNTs are employed, because the acidic oxygen-containing groups interact with basic amines [129, 130].

The effect of the oxidizing treatment varies significantly, depending on the CNT material used (SWNTs or MWNTs), the density of any structural defects, and the reaction conditions. The oxidation process starts on defects and at the tips of the CNTs, where the curvature-and thus reactivity-is high. Under strongly oxidizing conditions (high temperature and concentration), the reaction may also proceed at the basal planes for SWNTs, such that new defects will be created and at some point the SWNTs might be cut or even fully destroyed. In contrast, MWNTs are far less reactive, with minimal changes generally observed using Raman spectroscopy; this means that the oxidation takes place only on existing defects. Tessonnier et al. have recently shown that both the number and the nature of the oxygencontaining groups created with HNO3 change, depending on the graphitic character of the nanomaterial, and thus its density of defects [131]. This observation might provide new opportunities for the selective functionalization of CNTs via oxidation. Alternatively, any undesired groups could be removed by thermal treatment in a vacuum or an inert gas (see Section 1.1). The oxygen-containing groups each exhibit different thermal stabilities; typically, carboxylic acids will be lost between 400 and 650 K, while phenols are stable up to 800 K (Figure 1.11b). However, some of the groups might be reformed upon exposure to the air [132].



Figure 1.11 (a) The most common oxygen-containing functional groups which can coexist on the surface of oxidized CNTs; (b) The groups are lost as CO or as CO_2 during heating in inert gas. Thus, it is possible to quantify them by using temperature-programmed desorption (TPD).

1.7.2 Functionalization by Coupling Reactions

Grafting using organic chemistry coupling reactions represents the most exciting and promising functionalization technique. These procedures do not cause damage to the CNTs; rather, they are selective and the desired groups are bonded covalently to the CNT backbone by C–C bonds, thus reducing the risk of leaching. Many different reactions have been identified, the most interesting being

cycloaddition, for example Diels–Alder reactions. As with oxidation, the CNT carbon atoms must be prone to react, either because of strain in SWNTs or because they are located next to defects (localized C–C double bond).

1.7.3

Noncovalent Functionalization

Noncovalent functionalization relies on strong van der Waals interactions between the CNT surface and small PAHs, such as pyrene. The attachment takes place by π – π stacking, and the anchoring has been shown to be irreversible. As there are no covalent bonds between the addend and the CNT, its electronic structure will not be modified.

1.8 Conclusion and Outlook

The synthesis of carbon nanomaterials is an ever-developing field of research, with many materials already having exhibited encouraging results for major applications in the life sciences, such as cancer diagnosis and therapy. Although most studies have focused on CNTs (SWNTs, MWNTs, arrays), very promising results have also been obtained with nanodiamonds, while fullerenes might receive additional attention if their large-scale production issues were to be resolved. A strong collaboration between materials scientists and biologists is crucial to further optimize carbon nanomaterials, depending on their target applications. Knowledge regarding the real state of a surface and possible impurities in the raw material must be shared. The presence of metal impurities and carbonaceous debris (possibly PAHs), along with the limited industrial production of high-quality SWNTs and SWNTs arrays, clearly reduces the real potential of these materials. The possible CNT toxicity must first be investigated and its causes understood in order to modify the material accordingly, by acting directly on its synthesis. Until recently, transition-metal nanoparticles were believed to be a prerequisite for growing CNTs, with the presence of metal impurities in the product being unavoidable. More recently, however, SWNTs have been grown directly on silica and other oxides without the need for any metal, thus eliminating one potential source of toxicity. Similar progresses are foreseeable, not only to reduce the surface carbonaceous debris, but also to design CNTs with controlled length and chirality, depending on the target application.

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