

Methods for carbon nanotubes synthesis—review

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Carbon nanotubes (CNTs) have been under scientific investigation for more than fifteen years because of their unique properties that predestine them for many potential applications. The field of nanotechnology and nanoscience push their investigation forward to produce CNTs with suitable parameters for future applications. It is evident that new approaches of their synthesis need to be developed and optimized. In this paper we review history, types, structure and especially the different synthesis methods for CNTs preparation including arc discharge, laser ablation and chemical vapour deposition. Moreover, we mention some rarely used ways of arc discharge deposition which involves arc discharge in liquid solutions in contrary to standard used deposition in a gas atmosphere. In addition, the methods for uniform vertically aligned CNTs synthesis using lithographic techniques for catalyst deposition as well as a method utilizing a nanoporous anodized aluminium oxide as a pattern for selective CNTs growth are reported too.

1. Introduction

Carbon nanotubes (CNTs) belong to relatively new nanomaterials that have been publically known for almost twenty years, but their history is a little bit longer. Carbon nanotubes (CNTs) were firstly observed and described in 1952 by Radushkevich and Lukyanovich¹ and later in 1976 the single (or double) walled carbon nanotubes were observed by Oberlin *et al.*² In more recent history the discovery of CNTs is attributed to Iijima as the first scientist who described the multiwalled carbon nanotubes (MWNTs) preparation process after a random event during the test of a new arc evaporation method for C₆₀ carbon molecule fabrication in 1991.³ Although he was the first one who published in Nature new phenomena for many scientists, at the same time a small company in the USA was already able to produce defected carbon nanotubes called carbon fibrils using a chemical vapour deposition process. In 1993 another two separate works from Iijima *et al.* and Bethune *et al.* describing the growth process of single walled carbon nanotubes (SWNTs) were reported.^{4,5}

Structurally, SWNTs can be compared to “rolled up” one-atom-thick sheets of graphite called graphene (Fig. 1). The way the graphene is wrapped along the honeycomb graphene

structure is given by chiral vector \vec{C} which is a result of a pair (n, m) of integers that correspond to graphene vectors \vec{a}_1 and \vec{a}_2 . The principle of SWNT construction from a graphene sheet along the chiral vector \vec{C} is shown in Fig. 2. There are two standard types of SWNTs constructions from a single graphene sheet according to integers (n, m) . The $(n, 0)$ structure is called “zigzag” and the structure where $n = m$ (n, n) is called “armchair”. The third non-standard type of CNTs construction, which can be characterized by the equation where $n > m > 0$, is called “chiral”. The chirality predestinates the electrical, mechanical, optical and other properties of CNTs. For example Dresselhaus *et al.* reported how the chiral vector and the corresponding pairs of integers influence the electrical properties of CNTs.⁶

CNTs can be constructed in two basic forms, SWNTs and MWNTs. SWNTs consist of a single tube of graphene (Fig. 1), whereas MWNTs are composed of several concentric tubes of graphene fitted one inside the other. The diameter of CNTs varies from a few nanometres in the case of SWNTs to several tens of nanometres in the case of MWNTs. The lengths of the CNTs are usually in the micrometre range.⁷ The simplest example of MWNTs is double walled carbon nanotubes

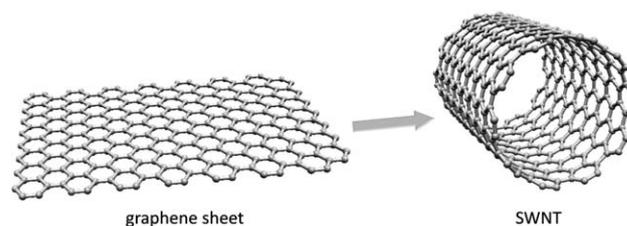


Fig. 1 Wrapping of graphene sheet to form SWNT.

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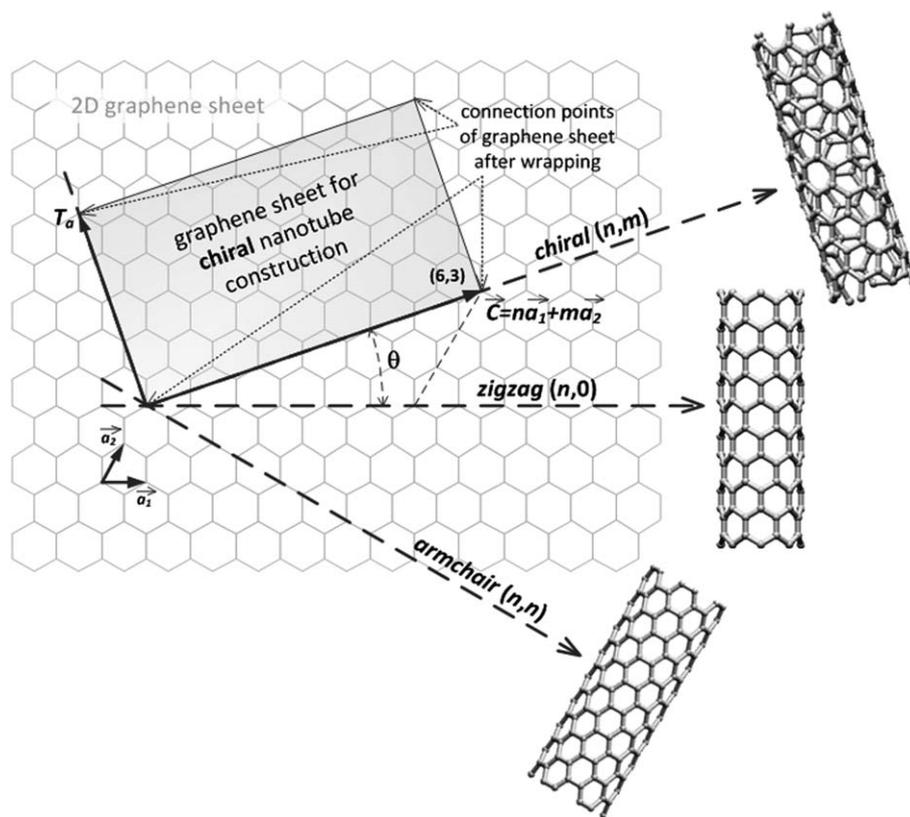


Fig. 2 The principle of CNT construction from graphene sheet along the chiral vector \vec{C} .

(DWNTs) as shown in the Fig. 3a. They provide a combination of outstanding properties of SWNTs and thus they have several advantages over simple SWNTs (*e.g.* higher stability and stiffness or independent doping of inner and outer tubes).⁸ The TEM image of MWNTs deposited using PECVD at atmospheric pressure is shown in Fig. 3b.

From the publication of Iijima's discovery,³ the CNTs have begun to be widely used in many applications due to their unique electrical, mechanical, optical, thermal and other properties. The application of CNTs is usually given by the CNTs structure (number of walls, diameter, length, chiral angle, *etc.*), which gives them the specific properties. The possible applications of CNTs include conductive films, solar cells, fuel cells, supercapacitors, transistors, memories, displays, separation membranes and filters, purification systems, sensors, clothes, *etc.*

The CNTs in sizeable quantities could be produced using various methods that are summarized in Fig. 4. Each of them has some advantages and disadvantages resulting in different growth

results, which predestinates a choice of specific method for preparation of CNTs with requested properties. The fact that a SWNT and a MWNT of the same length do not have the same weight has been neglected until now. Therefore, it is very important to establish the relationships between the weight and the density of CNTs and their geometrical characteristics (inner diameter, outer diameter, and number of walls).⁹ The diameter

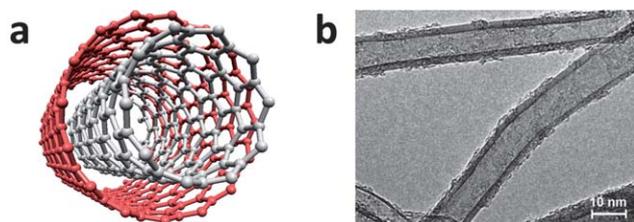


Fig. 3 (a) DWNT as a simplest example of MWNTs. (b) TEM image of MWNTs deposited using PECVD.



Fig. 4 Currently used methods for CNTs synthesis.

differences also affect the CNTs solubility in superacids and dispersibility in surfactants. Postprocessing such as purification also influences solubility of CNTs and must be controlled. For example Duque *et al.* showed that in oleum, the small-diameter SWNTs are more easily protonated and thus more soluble than larger ones. Regarding these results, the yield in single (*n,m*) SWNT-type separation can be increased. Moreover, they observed that solubility and dispersibility play key role for macroscopic SWNT processing techniques including fiber spinning, material reinforcement, and thin-film production.¹⁰ The aim of this study is to provide a short review about the current methods used for CNTs synthesis.

2. CNTs synthesis

High temperature preparation techniques such as arc discharge or laser ablation were first used to produce CNTs but nowadays these methods have been replaced by low temperature chemical vapour deposition (CVD) techniques (<800 °C), since the orientation, alignment, nanotube length, diameter, purity and density of CNTs can be precisely controlled in the latter.¹¹ The most utilized methods and some of other non-standard techniques like liquid pyrolysis and bottom-up organic approach are discussed below.

Most of these methods require supporting gases and vacuum, but the growth at atmospheric pressure has been already reported.^{12–16} However, gas-phase methods are volumetric and hence they are suitable for applications such as composite materials that require large quantities of nanotubes and industrial-scale synthesis methods to make them economically feasible. On the other hand, the disadvantages of gas-phase synthesis methods are low catalyst yields, where only a small percentage of catalysts form nanotubes, short catalyst lifetimes, and low catalyst number density.¹⁷

Whatever CNT preparation method is applied, the CNTs are always produced with a number of impurities whose type and amount depend on the technique used. Most of above mentioned techniques produce powders which contain only a small fraction of CNTs and also other carbonaceous particles such as nanocrystalline graphite, amorphous carbon, fullerenes and different metals (typically Fe, Co, Mo or Ni) that were introduced as catalysts during the synthesis. These impurities interfere with most of the desired properties of CNTs and cause a serious impediment in detailed characterisation and applications. Therefore, one of the most fundamental challenges in CNT science is the development of efficient and simple purification methods.¹⁸ Most common purification methods are based on acid treatment of synthesized CNTs.¹⁹

2.1 Arc discharge

Arc discharge belongs to the methods that use higher temperatures (above 1700 °C) for CNT synthesis which usually causes the growth of CNTs with fewer structural defects in comparison with other techniques.

2.1.1 MWNTs synthesis. The arc discharge synthesis of MWNTs is very simple in the case when all growth conditions are ensured. The most utilized methods use DC arc discharge between

two graphite usually water-cooled electrodes with diameters between 6 and 12 mm in a chamber filled with helium at subatmospheric pressure. Nevertheless, some other works with the use of hydrogen or methane atmosphere have been also reported. For example, Ebbesen and Ajayan use a variant of the standard arc-discharge technique also used by Iijima³ for fullerene synthesis under He atmosphere to obtain first large-scale synthesis of CNTs. Under certain conditions, a pure nanotube and nanoscale particles in high yield were obtained. The purity and yield depended sensitively on the gas pressure in the reaction vessel.²⁰ Wang *et al.* showed that different atmospheres markedly influence the final morphology of CNTs. They used DC arc discharge of graphite electrodes in He and methane. By evaporation under high pressured CH₄ gas and high arc current, thick nanotubes embellished with many carbon nanoparticles were obtained. On the other hand, thin and long MWNTs were obtained under a CH₄ gas pressure of 50 Torr and an arc current of 20 A for the anode with a diameter of 6 mm.²¹ Moreover, Zhao *et al.* found that the variation of carbon nanotube morphology was more marked for the case of evaporation in CH₄ gas than that in He gas.²² In different work, Zhao *et al.* used hydrogen gas atmosphere for preparation of fine and long MWNTs. By comparing with He and methane gases, a very big difference was found. Namely, little carbon smoke occurred in H₂ gas, but much more carbon smoke was observed for the evaporation in CH₄ and He gases.²³ Later they showed that evaporation of graphite electrodes in H₂ gas by DC arc discharge forms not only fine and long MWNTs but also graphene sheets deposited on the cathode.²⁴ Shimotani *et al.* reported synthesis of MWNTs using an arc discharge technique under He, ethanol, acetone and hexane atmosphere at various pressures (from 150 to 500 Torr). They concluded that arc discharges in the three organic atmospheres (ethanol, acetone and hexane) produce more MWNTs, by two times at least, than those in the He atmosphere. This can be explained as follows: contrary to helium, the acetone, ethanol and hexane can be ionized and the molecules can be decomposed into hydrogen and carbon atoms. These ionized species may contribute the synthesis of MWNTs, so the higher yield of CNTs is produced. They showed that in all the cases of organic molecular atmospheres, yields of MWNTs increase as the pressure increases up to 400 Torr.²⁵ Jiang *et al.* studied the influence of NH₃ atmosphere on the arc-discharge growth of CNTs and demonstrating that the arc-discharge method in NH₃ atmosphere is one highly efficient method for CNTs preparation. They concluded that there is no significant difference of the shapes and the structures between NH₃ atmosphere and other atmospheres such as He, H₂, *etc.*²⁶ The consumption of anode during the process is faster than the growth of MWNTs layer on the cathode. Therefore the gap between the electrodes of 30 to 110 mm² surface area has to be held in the desired distance during the growth process (usually between 1 and 4 mm). This is ensured by one electrode constant feed that leads to a high yield and stable arc discharge growth process.

The arc discharge deposition is usually done as a DC arc discharge, but pulsed techniques were also reported. For example Parkansky *et al.* reported single-pulse arc production of near vertically oriented MWNTs deposited on the Ni/glass samples using a graphite counter-electrode in ambient air. MWNTs (typically 5–15 walls) with a diameter of about 10 nm and lengths of up to 3 μm were produced on the samples with a single 0.2 μs

pulse.²⁷ Tsai *et al.* also used single-pulse discharge in air. They obtained MWNTs with the outer diameter of 17 nm and an inner diameter of 5 nm using a peak current of 2.5 A and a discharging time of 1000 μ s.²⁸

Arc discharge is usually used for some non-standard CNTs deposition. Contrary to standard MWNTs deposition using a gas atmosphere there were reported several works involving arc discharge in liquid solutions. Jung *et al.* reported high yield synthesis of MWNTs by arc discharge in liquid nitrogen. They concluded that this technique can be a practical option for the large-scale synthesis of MWNTs with high purity.²⁹ A similar method was also used for MWNTs deposition by Sornsuwit and Maaithong³⁰ Montoro *et al.* reported the synthesis of high-quality SWNTs and MWNTs through arc-discharge in H₃VO₄ aqueous solution from pure graphite electrodes. DC arc discharge was generated between two high purity graphite electrodes. The high-resolution TEM images clearly showed that MWNTs are highly crystalline, with a well-ordered structure and free of defects. They obtain MWNTs with an outer diameter of 10–20 nm and an interlayer distance of approximately 0.35 nm between graphene layers.³¹ MWNTs were also synthesized in high yield by arc discharge in water between pure graphite electrodes by Guo *et al.*³² The production of carbon nanomaterials by arc discharge under water or liquid nitrogen was also reported by Xing *et al.*³³

2.1.2 SWNTs synthesis. The arc discharge deposition of CNTs could be done without use of or with use of different catalyst precursors. Usually the MWNTs are produced when no catalyst is used. On the other hand, the SWNTs are produced when the transition metal catalyst is used. The process of SWNTs growth in arc discharge utilizes a composite anode, usually in hydrogen or argon atmosphere. The anode is made as a composition of graphite and a metal, such as Ni, Fe, Co, Pd, Ag, Pt, *etc.* or mixtures of Co, Fe, Ni with other elements like Co–Ni, Fe–Ni, Fe–No, Co–Cu, Ni–Cu, Ni–Ti, *etc.* The metal catalyst plays a significant role in the process yield. To ensure high efficiency, the process also needs to be held on a constant gap distance between the electrodes which ensures stable current density and anode consumption rate. In this process, unwanted products such as MWNTs or fullerenes are usually produced too.

Firstly, the SWNTs growth process was described in two separate works by Iijima and Ichihashi⁴ who presented SWNTs of 1 nm and Bethune *et al.* who described Co catalyzed growth of SWNTs. Bethune *et al.* reported that co-evaporation of carbon and cobalt in an arc generator leads to the formation of carbon nanotubes with very small diameters (about 1.2 nm) and walls made of a single atomic layer thick only.⁵ Ajayan *et al.* also use Co catalyst for SWNTs synthesis of 1–2 nm diameter using arc discharge in He atmosphere.³⁴ One of the most utilized catalysts for SWNTs synthesis is nickel. Seraphin *et al.* studied the catalytic role of Ni, Pd, and Pt in the formation of carbon nanoclusters using DC arc discharge operated at 28 V, 70 A, and under a 550 Torr He atmosphere. They found out that nickel-filled anode stimulated the growth of SWNTs.³⁵ A similar method was used by Saito *et al.* who reported SWNTs growing radially from Ni fine particles.³⁶ Zhou *et al.* reported radially grown SWNTs synthesized using yttrium carbide loaded anode.³⁷ In 1996 Saito *et al.* reported the investigation of single-

layered nanotubes produced with platinum-group metals (Ru, Rh, Pd, Os, Ir, Pt) using arc discharge. They reported that Rh, Pd, and Pt showed catalytic activity for growing SWNTs, but the other metals did not. Bundles of dense SWNTs with diameter 1.3–1.7 nm were extruding radially from metal particles for Rh and Pd; the sizes of core particles were 20–30 nm for Rh and 50–200 nm for Pd. In the case of Pt, one or few SWNTs (typically 1.3–2.0 nm in diameter and sometimes similar to 3 nm) grew from a tiny particle (of about 10 nm).³⁸ In another work, Saito *et al.* reported SWNTs produced by the arc discharge method with Fe, Co, Ni, F/Ni, La, and Ce catalysts. According to growth patterns and morphology of SWNTs, they divided the synthesis results into three groups: the tubes tangled with each other to form “highway junction” pattern for Co and Fe/Ni, long and thin tubes radially growing from Ni particles, and short and thick tubes growing from lanthanide compound particles.³⁹

The arc discharge method is still in use for SWNTs synthesis, but usually with a new approach. Chen *et al.* reported the FH (ferrum–hydrogen) arc discharge method. Using this method, SWNTs are produced by a hydrogen DC arc discharge with evaporation of carbon anode containing 1% Fe catalyst in H₂–Ar mixture gas. The as-grown SWNTs have high crystallinity. An oxidation purification process of as-grown SWNTs with H₂O₂ has been developed to remove the coexisting Fe catalyst nanoparticles. As a result, SWNTs with purity higher than 90% have been achieved.^{40,41} Fan *et al.* looked for a cheap method for SWNTs synthesis. They successfully produced SWNTs in argon DC arc discharge from charcoal as carbon source and FeS (20 wt %) as catalyst. According to SEM, TEM and Raman analysis, they achieved high purity SWNTs with diameter of about 1.2 nm. By this easy-to-get and relatively low cost material, the experimental results clearly indicated that charcoal has the opportunity of reducing the cost of SWNTs production.⁴² In another work, Wang *et al.* studied the role of Mo on the growth of SWNTs in the arc discharge method. They incorporated Mo into Ni/Y–He and Fe–Ar/H₂, which are two typical arc systems. In both systems Mo dramatically increased the yield of soot. The authors found that the purity of SWNTs did not change effectively for the Ni–Y/Mo–He system with the addition of Mo, but noticeable increment of purity was observed for Fe/Mo–Ar/H₂ system.⁴³ Li *et al.* presented a possibility of SWNTs synthesis in air by pulsed arc discharge by preheating the catalyst to 600 °C as an optimum that assists with the synthesis of SWNTs in air under pressure of 5–10 kPa. The SWNTs had a diameter of 1.5–2 nm and reached the length of several micrometres.⁴⁴

2.1.3 DWNTs synthesis. The process of DWNTs deposition is more complicated than the production of SWNTs and MWNTs, but several successful attempts at methods for their preparation using arc discharge have been reported. Hutchison *et al.* first reported DWNTs an arc discharge technique in a mixture atmosphere of argon and hydrogen.⁴⁵ The anode was a graphite rod of 8.2 mm in diameter filled with catalyst. A mixture of Ni, Co, Fe and S was used as the catalyst. The obtained DWNTs formed into bundles as a rule. Occasionally, SWNTs were observed as a by-product. Sugai *et al.* reported new synthesis of high-quality DWNTs by the high-temperature pulsed arc discharge method using Y/Ni alloy catalysts.⁴⁶

Later, more sophisticated methods for DWNTs of higher quality appeared. DWNTs super bundles grown selectively above a bowl-like cathode by arc discharge in a hydrogen-free atmosphere were reported by Huang *et al.*⁴⁷ Their DWNTs can resist high-temperature (up to 720 °C) oxidation in air without additional annealing even after acid treatment. This can be explained by an *in situ* defect-healing effect of the bowl-like cathode and the absence of reactive gases during arc discharge. Synthesis of DWNTs from coal in hydrogen-free atmosphere was also reported by Qiu J.S. *et al.*⁴⁸

Qiu HX *et al.* reported highly efficient and high scale synthesis of relatively perfect structural integrity DWNTs by an arc discharge method using trace halide (particularly potassium chloride) as a promoter in an iron sulfide catalyst.⁴⁹ Both as-synthesized DWNTs and purified DWNTs resisted to high temperature oxidation. It was proved that potassium chloride is a crucial factor for high yield formation of DWNTs with fewer defects. Another work by Liu *et al.* reported preparation of DWNTs using nickel formate dihydrate as an effective catalyst precursor for selectively synthesizing DWNTs with excellent oxidation resistance up to 800 °C using a hydrogen arc discharge technique.⁵⁰

The synthesis of DWNTs from MWNTs by hydrogen arc discharge was reported by Li *et al.* DWNTs were synthesized in a large scale using graphite powders or MWNTs/carbon nanofibers as carbon source. They found that their DWNT product had higher purity than that from graphite powders. The results from HRTEM observations revealed that more than 80% of the CNTs were DWNTs and the rest were SWNTs. It was observed that the ends of the isolated DWNTs were uncapped and it was also found that cobalt as the dominant composition of the catalyst played a vital role in the growth of DWNTs by this method.⁵¹

The general problem of produced CNTs is the presence of impurities that usually influence the final properties of CNTs as a material that could be used in some special application. Therefore, several papers reported on dealing with this problem. Acidic and thermal treatment, annealing, oxidation, filtration, ultrasonication and other techniques are used for CNTs purification. For example Ando *et al.* reported that easy purification of the MWNTs prepared by DC arc discharge of graphite electrodes in H₂ gas could be done by removal of coexisting carbon nanoparticles using infrared irradiation in a heating system in air at 500 °C for 30 minutes.⁵² The effect of calcination at different temperatures ranging from 300 to 600 °C on MWNTs produced by DC arc discharge was studied by Pillai *et al.* They found that calcination in air at 400 °C for 2 hours is an efficient and simple method to eliminate carbonaceous impurities from the nanotube bundles with minimal damage to the tube walls and length.⁵³ The issue of CNT purification represents a wide field of investigation and reviews of CNTs purification have been already published, *e.g.* in ref. 54–57.

2.2 Laser ablation

The properties of CNTs prepared by the pulsed laser deposition process (PLD) are strongly dependent on many parameters such as: the laser properties (energy fluence, peak power, cw *versus* pulse, repetition rate and oscillation wavelength), the structural

and chemical composition of the target material, the chamber pressure and the chemical composition, flow and pressure of the buffer gas, the substrate and ambient temperature and the distance between the target and the substrates.

Laser ablation, as crucial step of PLD, is one of the superior methods to grow SWNTs with high-quality and high-purity. In this method, which was first demonstrated by Smalley's group in 1995,⁵⁸ the principles and mechanisms are similar to the arc discharge with the difference that the energy is provided by a laser hitting a graphite pellet containing catalyst materials (usually nickel or cobalt).⁵⁹ Almost all the lasers used for the ablation have been Nd:YAG and CO₂. For example, Zhang *et al.* prepared SWNTs by continuous wave CO₂ laser ablation without applying additional heat to the target. They observed that the average diameter of SWNTs produced by CO₂ laser increased with increasing laser power.^{60–62}

Until now, the relationship between the excitation wavelength and the growth mechanisms of SWNTs has not been clarified. It may be expected that a UV laser creates a new species of nanoparticles and suggests a new generation mechanism of CNTs because the UV laser is superior in the photochemical ablation to the infrared laser which is effective for photothermal ablation. Lebel *et al.* synthesized SWNTs using the UV-laser (KrF excimer) ablation of a graphite target appropriately doped with Co/Ni metal catalyst.⁶³ In their work, they tested as-prepared SWNTs as a reinforcing agent of polyurethane. Kusaba and Tsunawaki used XeCl excimer laser with the oscillation wavelength of 308 nm to irradiate a graphite containing Co and Ni at various temperatures and they found that laser ablation at 1623 K produced the highest yield of SWNTs with the diameter between 1.2 and 1.7 nm and the length of 2 μm or above.⁶⁴

Recently, Stramel *et al.* have successfully applied commercial MWNTs and MWNTs–polystyrene targets (PSNTs) for deposition of composite thin films onto silicon substrates using PLD with a pulsed, diode pumped, Tm:Ho:LuLF laser (a laser host material LuLF (LuLiF₄) is doped with holmium and thulium in order to reach a laser light production in the vicinity of 2 μm).⁶⁵ They found that usage of pure MWNTs targets gives rise to a thin film containing much higher quality MWNTs compared to PSNTs targets. Similarly, Bonaccorso *et al.* prepared MWNTs thin films deposited by PLD techniques (with Nd:YAG laser) ablating commercially polystyrene-nanotubes pellets on alumina substrates.⁶⁶

2.3 Chemical vapour deposition

Catalytic chemical vapour deposition (CCVD)—either thermal⁶⁷ or plasma enhanced (PE)—is now the standard method for the CNTs production. Moreover, there are trends to use other CVD techniques, like water assisted CVD,^{68–70} oxygen assisted CVD,⁷¹ hot-filament (HFCVD),^{72,73} microwave plasma (MPECVD)^{74,75} or radiofrequency CVD (RF-CVD).⁷⁶ CCVD is considered to be an economically viable process for large scale and quite pure CNTs production compared with laser ablation. The main advantages of CVD are easy control of the reaction course and high purity of the obtained material, *etc.*⁷⁷

The CNT growth model is still under discussion. Recently, Fotopoulos and Xanthakis discussed the traditionally accepted models, which are base growth and tip growth. In addition, they

mentioned a hypothesis that SWNTs are produced by base growth only, *i.e.* the cap is formed first and then by a lift off process the CNT is created by addition of carbon atoms at the base. They refer to recent *in situ* video rate TEM studies which have revealed that the base growth of SWNT in thermal CVD is accompanied by a considerable deformation of the Ni catalyst nanoparticle and the creation of a subsurface carbon layer. These effects may be produced by the adsorption on the catalyst nanoparticle during pyrolysis.⁷⁸ In order to produce SWNTs, the size of the nanoparticle catalyst must be smaller than about 3 nm.

The function of the catalyst in the CVD process is the decomposition of carbon source *via* either plasma irradiation (plasma-enhanced CVD, PECVD) or heat (thermal CVD) and its new nucleation to form CNTs. The most frequently used catalysts are transition metals, primarily Fe, Co, or Ni.⁷⁹ Sometimes, the traditionally used catalysts are further doped with other metals, *e.g.* with Au.⁸⁰ Concerning the carbon source, the most preferred in CVD are hydrocarbons such as methane,⁸¹ ethane,⁸² ethylene,⁸³ acetylene,⁸⁴ xylene,^{85,86} eventually their mixture,⁸⁷ isobutane⁸⁸ or ethanol.^{89,90} In the case of gaseous carbon source, the CNTs growth efficiency strongly depends on the reactivity and concentration of gas phase intermediates produced together with reactive species and free radicals as a result of hydrocarbon decomposition. Thus, it can be expected that the most efficient intermediates, which have the potential of chemisorption or physisorption on the catalyst surface to initiate CNT growth, should be produced in the gas phase.⁹¹

Commonly used substrates are Ni, Si, SiO₂, Cu, Cu/Ti/Si, stainless steel or glass, rarely CaCO₃; graphite and tungsten foil or other substrates were also tested.^{92,93} A special type of substrate, mesoporous silica, was also tested since it might play a templating role in guiding the initial nanotube growth. For example, Zhu *et al.* reported a CCVD synthesis of DWNTs over supported metal catalysts decomposed from Fe and Co on mesoporous silica. They obtained bundles of tubes with a relatively high percentage of DWNTs in areas where tubular layered structures could be clearly resolved. Moreover, the crystal-like alignment of very uniform DWNTs was observed.⁹⁴ Similarly, Ramesh *et al.* succeeded in high-yield selective CVD synthesis of DWNTs over Fe/Co loaded high-temperature stable mesoporous silica.⁹⁵ Another substrate, zeolites, was studied by Hiraoka *et al.* They used CCVD of acetylene over well-dispersed metal particles (typically Co/Fe binary system) embedded in heat-resistant zeolites at temperatures above 900 °C for selective synthesis of DWNTs.⁹⁶

The choice of catalyst is one of the most important parameters affecting the CNTs growth. Therefore, its preparation is also a crucial step in CNTs synthesis. The influence of the composition and the morphology of the catalyst nanoparticles on CNTs growth by CVD are summarized in a review paper.⁹⁷ Flahaut *et al.* reported the influence of catalyst preparation conditions for the synthesis of CNTs by CCVD. In their work, the catalysts were prepared by the combustion route using either urea or citric acid as the fuel. They found that the milder combustion conditions obtained in the case of citric acid can either limit the formation of carbon nanofibers or increase the selectivity of the CCVD synthesis towards CNTs with fewer walls, depending on the catalyst composition.⁹⁸ Xiang *et al.* prepared CNTs *via* CCVD of acetylene on a series of catalysts derived from Co/Fe/Al layered double hydroxides (LDHs). They observed that the

content of Co in the precursors had a distinct effect on the growth of CNTs. Increasing Co content enhanced the carbon yield, due to good dispersion of a large number of active Co species. Higher Co content led to the formation of CNTs with smaller diameters and less structural disorder.⁹⁹

Lyu *et al.* produced high-quality and high-purity DWNTs by catalytic decomposition of benzene as an ideal carbon source and Fe–Mo/Al₂O₃ as a catalyst at 900 °C. They obtained DWNTs bundles free of amorphous carbon covering on the surface and of a low defect level in the atomic carbon structure.¹⁰⁰ Zhang *et al.* prepared MWNTs with diameters of 40–60 nm by the catalytic decomposition of methane at 680 °C for 120 min, using nickel oxide–silica binary aerogels as the catalyst.^{101,102} Sano and colleagues evaluated two systems of metallic catalyst/carbon sources for CNTs growth: ethanol/Co and benzene/Fe. Moreover, they investigated the effects of two different reactors (gas-flow reactor and a submerged-in-liquid reactor) on the quality of CNTs.¹⁰³ Jiang *et al.* studied the growth of CNTs *in situ* on the pretreated graphite electrode (GE) *via* CCVD using Ni(NO₃)₂ as the catalyst.¹⁰⁴ The prepared CNTs had 80 and 20 nm in outer and inner diameter, respectively. Moreover, the CNTs were not very long (compared with data reported elsewhere): their length was from about 200 to 1000 nm as a result of shorter growing time. Scheibe *et al.* tested Fe and Co for MWNTs fabrication. Additionally, the authors were interested in concentrations of the carboxyl and hydroxyl groups on the carbon nanotube surface, which are essential features for applications in many science branches such as nanomedicine, biosensors or polymer nanocomposites.¹⁰⁵

Feng *et al.* used acetone as a carbon source, ferrocene as source of Fe catalyst and thiophene as promoter to synthesize high-quality DWNTs thin-films in a one-step CCVD reaction process in an argon flow.¹⁰⁶ Li studied the synthesis of well aligned MWNTs on a large area of Ni deposited SiO₂/Si substrates *via* the pyrolysis of C₂H₂ using the thermal CVD technique at 900 °C. He found that NH₃ pretreatment was very crucial to control the surface morphology of catalytic metals and thus to achieve the vertical alignment of CNTs. With a higher density of Ni particles, better alignment of the CNTs can be obtained due to a steric hindrance effect between neighbouring CNTs. The degree of crystallization of the CNTs increased with increasing NH₃ pretreatment time. Energy dispersive X-ray spectrum analysis revealed that CNTs grew by a tip growth mechanism.¹⁰⁷ Liu and colleagues recently published the comprehensive review dealing with direct CVD growth of aligned, ultralong SWNTs on substrate surfaces, which are attractive building blocks for nanoelectronics. They discussed the key technical points, mechanisms, advantages, and limitations of this method.¹⁰⁸

Kim *et al.* reported a novel method for the growth of CNTs that uses three different iron-containing proteins: hemoglobin, myoglobin, and cytochrome c in order to control precisely the size and atomic structure of the CNTs. These iron-containing proteins were strongly adsorbed onto amine-terminated self-assembled monolayer (SAM) surfaces by peptide bonds between the carboxyl groups of the proteins and the amine groups of the SAMs, and used directly as catalysts in the synthesis of CNTs. Although this study has demonstrated the growth of MWCNTs from iron-containing proteins, the authors suggest that this method can also be applied to the synthesis of SWCNTs.¹⁰⁹

Cui *et al.* synthesized thin-walled, open-ended, and well-aligned N-doped CNTs on the quartz slides using acetonitrile as the carbon source and ferrocene as the catalyst. These free-standing films can be transferred easily to other substrates, which might be helpful to their applications in many fields. The products possessed large thin-walled index (TWI, the ratio of inner diameter and wall thickness of a CNTs). The authors investigated the effect of temperature on the growth of CNTs and they found that the diameter and the TWI of CNTs increase while the Fe encapsulation in CNTs decreases as the growth temperature rises in the range of 780–860 °C.¹¹⁰

Grazhulene *et al.* prepared CNTs by CCVD using ethanol vapour as the carbon source and Ni as the catalyst. The authors studied a correlation between the temperature of synthesis and CNTs ability for the modification of oxidation under various conditions. They demonstrated the CNTs adsorption capacity to a number of metal ions (Ag, Cu, Pb, Cd, Zn, Fe and Mg) regarding pH bath and element concentration in the solution. It was found that CNTs synthesized at 400 °C and treated with conc. HNO₃ in an autoclave at 110–120 °C possessed the maximum adsorption capacity of all studied elements, which exceeds the capacity of active coal, traditionally used for these purposes, by several times. The attained adsorption capacity is 5–10 times higher than that reported in the literature for CNTs in relation to the same elements. Thus, these CNTs seem to be suitable as collectors for the preconcentration of trace impurities in spectroscopic methods of analysis.¹¹¹

Du *et al.* synthesized CNTs by Co/MgO catalysed pyrolysis of dimethyl sulfide (C₂H₆S) at 1000 °C, which is rarely used as carbon source. The presence of sulfur can promote the growth of long SWNTs or branched CNTs (BNTs). They found that C₂H₆S vapour concentration as well as flow rate in the reaction chamber determine the quality of the product. The authors also proposed the detailed growth mechanism of BNTs which were formed at high flow rate of C₂H₆S vapour.¹¹²

2.3.1 PECVD. Plasma enhanced chemical vapour deposition (PECVD) is a suitable method for synthesis of CNTs hybrid materials and modification of their surface properties. Lim *et al.* reviewed the application of PECVD in the production and modification of CNTs. They emphasize the usage of the PECVD method for SWNTs growing at low temperatures and make an effort to better understand plasma chemistry and modelling.¹¹³ An example of the MWNTs forest-like structure deposited on solid substrate using PECVD is shown in Fig. 5.

PECVD can be also used in several different modes: radio frequency (RF-PECVD), direct current (DC-PECVD), diffusion (DPECVD) or microwave (MWPECVD). Kim and Gangloff demonstrated the low-temperature (480–612 °C) synthesis of CNTs on different metallic underlayers (*i.e.* NiV, Ir, Ag, Pt, W, and Ta) using DPECVD. They used an Fe/Al bilayer as the catalyst.¹¹⁴ Wang and Moore prepared vertically aligned CNTs using FeNi or Fe sputtered catalyst layers on glass substrates by RF- or DC-PECVD. They compared the CNTs growth mechanisms using both methods with respect to gas flow rate, plasma power and catalysts. They explained why RF-PECVD provided more efficient decomposition of gas molecules than DC-PECVD by plasma theory. The major difference between RF- and DC-PECVD was the higher concentration of reactive radicals in the

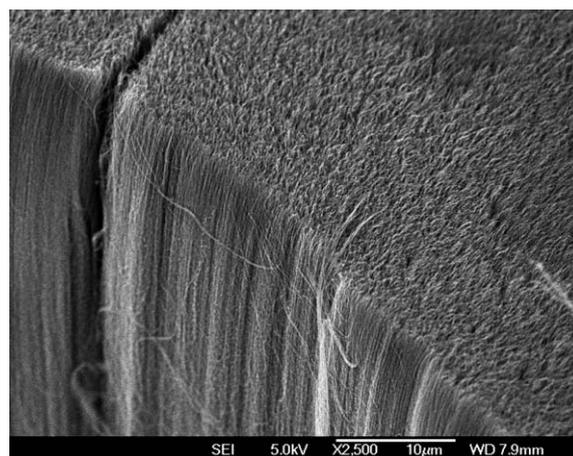


Fig. 5 SEM image of MWNTs forest deposited using PECVD at atmospheric pressure.

former. However, in DC-PECVD, the CNT growth was well aligned vertically. They found that FeNi thin film catalysts exhibited higher activity and better wetting ability than the Fe island thin film catalysts.¹¹⁵

Like in thermal CVD, numerous catalyst types to improve the yield and the quality of CNTs production are also applied in PECVD. For example, Luais *et al.* prepared spherical Ni nanoparticles film Ni(NO₃)₂ as a starting material, which was used as a catalyst. The diameter of Ni nanoparticles was about 50 nm. This catalyst was further used for synthesis of vertically aligned CNTs by PECVD in an electron cyclotron resonance chamber using a gas mixture of C₂H₂/NH₃ at 520 °C. The average thickness of the CNTs film was about 1 µm and the CNTs diameter was around 50 nm. After CNTs preparation, their surface was functionalized with oxygenated and aminated groups using microwave plasma to make them suitable for future bio-sensing applications. Moreover, they found that the plasma treatment was a very effective way to retain the CNTs aligned forest structure of electrode surface.¹¹⁶ He *et al.* focused their study on a TEM investigation of the crystallography of Ni catalysts for the vertical growth of carbon nanofibers (CNFs), which were synthesized by DC PECVD in an atmosphere composed of isopropyl alcohol and water.^{11,117} Yung and colleagues tested the influence of four types of substrates, namely Si, n++ Si, p++ Si and SiO₂, on CNTs growth on the Ni catalyst layer using PECVD. They found that the type of Si substrate has significant effects on CNT growth characteristics.¹¹⁸ Sun *et al.* studied the effect of catalyst film (Ni or Fe) thickness on vertically aligned CNTs growth by PECVD on different metal underlayers (Ti, Cr or Al) deposited on Si wafers. They found a critical thickness of about 10 nm of Fe or Ni catalyst film is needed to grow CNTs on various underlayer metals. They observed that average diameter, diameter distribution, density, growth rate and contact resistance exhibited strong correlation with the choice of catalyst/underlayer combination.¹¹⁹

Häffner *et al.* demonstrated the fabrication of a biocompatible system of CNTs electrodes by PECVD using ferritin as the catalyst material. Ferritin consists of a small Fe₂O₃ compound core with a diameter in the nanometre range, enclosed by a protein shell a few nanometres thick. Treated with oxygen

plasma, amino acids around the ferritin cores were removed, the iron cores were automatically separated from each other and dense vertically aligned CNTs grew from the well separated iron cores. For possible application of these CNTs electrodes in neuroimplants, which is based on flexible temperature sensitive substrates (like artificial mica), it is important to reach low temperatures during the preparation process (down to 450 °C).¹²⁰

Pd was also tested as a catalyst material in the work of Vollebregt *et al.*, who prepared vertically self-aligned CNTs and CNFs. The authors compared two preparation methods with various conditions and catalysts (Pd, Ni, Fe, Co) as follows: PECVD at 450 °C to 500 °C and atmospheric-pressure chemical vapour deposition (APCVD) between 450 °C and 640 °C. High-density self-aligned CNTs were obtained using APCVD and Pd as the catalyst, while Co and Fe resulted in random growth. TEM revealed that the CNTs grown by Pd with PECVD formed large bundles of tubes, while Ni formed large-diameter CNFs. The authors found that the CNTs grown using Pd or Ni were of low quality compared with those grown by Co and Fe.¹²¹

However, some works were published with no usage of catalysts for CNTs growing. Qu and colleagues prepared new hybrid material consisting of spontaneous assembly of carbon nanospheres on aligned or nonaligned SWNTs using the PECVD method. The carbon nanospheres were formed with a uniform size of 30–60 nm. The formation of these spheres is a catalyst-free process and strongly depends on the applied plasma power and other factors. This heterojunction structure based on different types of carbon seems to be promising as a building complex system for various applications.¹²²

Analogous to various catalysts, different substrates for CNTs preparation can be also used in the PECVD process. For example, Duy *et al.* reported the fabrication of CNTs on Ni-coated stainless steel or Si substrates using DC-PECVD. The synthesized CNTs have a diameter of about 30 nm and a length of about 1.2 μm. They found that CNTs grown on the stainless steel substrates were more uniform compared with those grown on the Si substrates. Moreover, they showed the potential of CNTs in field emission applications, especially CNT-based cold-cathode X-ray tubes.¹²³

Jang and Ahn fabricated flexible thin film transistors (TFT) with randomly oriented single-walled SWNTs, which were synthesized selectively on a designed array of catalyst photore-sists using the PECVD method. The process involves SWNTs growth on SiO₂/Si substrates. This might be of interest for various applications of SWNTs in flexible electronics.¹²⁴ Ono *et al.* also prepare TFT with a carbon CNTs network as a channel using grid-inserted PECVD.¹²⁵ Yang *et al.* synthesized two types of hybrid carbon materials by RF-PECVD: the tree-CNTs with branches of different diameters using ferrocene powder as the catalyst and the wing-like CNTs with graphitic-sheets of different densities using Co or Ni thin film coated on the surface of Ti thin film (20 nm). In both cases, Si(100) was used as the substrate. They found that both the tree- and wing-like CNTs exhibited lower turn-on field and higher emission current density than the pristine CNTs, which can be ascribed to the effects of branch size, crystal orientation, and graphitic-sheet density.¹²⁶ Seo *et al.* investigated the growth of metal-free MWNTs on Corning glass substrates with a microwave PECVD (MPECVD) method using methane and hydrogen gases. An amorphous

carbon layer deposited with RF magnetron sputtering was used as a catalyst to grow metal-free CNTs. The catalyst layer was pretreated using H₂ plasma at 600 °C for 3 min and the CNTs grew with the different thickness of the catalyst layer for 30 min at 600 °C.¹²⁷ Bu and Oei also used Corning glass as a substrate for vertically aligned CNTs deposition using PECVD. MWNTs grew by flow carbon-containing gas over silicon substrates coated with Ni catalyst and indium tin oxide diffusion barrier at temperature over 700 °C. They functionalized the CNTs surface with 1*H*,1*H*-2*H*,2*H* perfluorodecyl-trichlorosilane and hexane mixture in order to provide protective hydrophobic surface coating. Such self-cleaning CNTs coated glass is ideal for UV-blocking applications, such as UV inhibitors in windows.¹²⁸

A reproducible high-yield purification process of MWNTs by thermal annealing in ultrapure oxygen was developed by Bu, who prepared vertically aligned MWNTs by PECVD, using acetylene and ammonia at 650 °C.¹²⁹

2.3.2 CVD methods for uniform vertically aligned CNTs

synthesis. The growth of vertically aligned carbon nanotube forests is studied extensively because it represents one of the highest yield methods of nanotube growth.¹³⁰ The aim of several works is to fabricate vertically aligned CNTs with homogeneous distribution on the surfaces and high uniformity. It is evident to use nanolithography to create pattern of the catalyst on the surface on which CNTs are formed using CVD methods. In the work of Kim *et al.*, the Si wafer was used as a substrate and Ni as a catalyst deposited on a diffusion barrier from Ni/Ti. Ni dots catalyst of 1.6 μm and about 200 nm was patterned using UV and e-beam lithography, respectively. The method of CNTs formation uses the triode PECVD reactor with gas ratio C₂H₂/(H₂ or NH₃) at 620 °C. The positive ions in the cathode sheath of the plasma can force the CNTs to grow perpendicular to the substrate. The diameter of created CNTs depended on Ni dots size.¹³¹

Yamada *et al.* used high efficiency water-assisted CVD synthesis of vertically aligned DWNTs forests with heights of up to 2.2 μm using Fe catalyst. They achieved CNTs with a carbon purity of 99.95%.¹³²

Very interesting methods are the ones which use non-lithographic techniques. The most frequently used method of aligned CNTs formation (Fig. 6) is the usage of nanoporous anodized aluminium oxide (AAO) as template for CNTs growth. In the work of Kim *et al.*,¹³³ the CNTs were grown on AAO/Si substrate. A catalytic metal layer was formed on the Si wafer by direct deposition. Two types (A and B) of nanoporous aluminium templates were used for the study of the growth characteristics of CNTs. Type A was aluminium of 500 nm thickness, which was deposited on a silicon wafer. Type B was aluminium on Co-coated silicon wafer. The thickness of the Co-layer was 100 Å. The pore diameter and pore depth was approximately 33 nm and 210 nm for Type A and 5 nm and 220 nm for Type B, respectively. After the pore widening process, the pore was enlarged to approximately 60 nm and 33 nm for Type A and Type B, respectively. The CNTs growth was carried out on the AAO at temperature below 550 °C by DC-PECVD. An acetylene gas was used as a carbon source and an ammonia gas was used as a dilution and catalytic gas. The DC plasma was applied to grow vertically aligned CNTs. The CNT growth with PECVD on Type A was quite different from the CNT growth

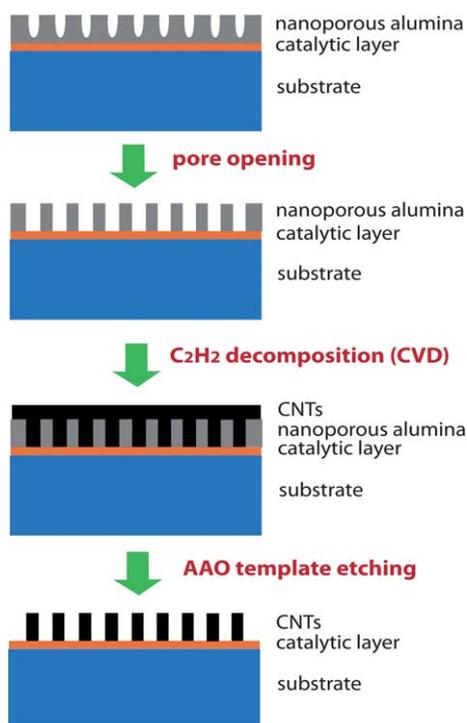


Fig. 6 Process of CNTs growth using the AAO template.

with thermal CVD because CNTs were not grown on the AAO/Si barrier. Graphitization of the CNTs was very poor compared to the CNTs grown on glass substrate using thermal CVD. The CNTs grown on the barrier between pores do not look like nanotubes but carbon nanofibers. In the case of Type B the length of CNT is almost the same as the pore depth because CNTs did not grow on the AAO/Si barrier, but only on the catalyst on the bottom of the pores. CNTs grew on AAO/Si without a catalyst, while there was no overgrowth of CNTs on AAO/Si with a catalyst. In synthesis of CNTs using AAO template with/without a Co layer, both alumina and Co can work as a catalyst with flowing acetylene.

Similar work employing CVD on an AAO template is described by Sui *et al.*¹³⁴ The authors found the pores in templates had diameters of 24 nm and 86 nm according to the anodizing voltage and acid used. Porous anodic alumina film in this case also acts as both the catalyst and the template in the formation of CNTs by thermal decomposition of acetylene. The MWNTs grew by CVD in a tubular stove with a gas-flow mixture of N₂/C₂H₂ (90 : 10) with a rate of 100 ml min⁻¹ for 2 h at 650 °C. The walls of both CNTs types consisted of numerous stacked flakes, which is different from that of MWNTs made by arc-discharging and other CVD methods. Both kinds of CNTs had the same wall structures. After treatment of templates in boiling water before CVD, different results were obtained. The CNTs with the bamboo-like appearances grow from the template with 24 nm pore diameter. However solid carbon nanofibers rather than CNTs were obtained in the template with 86 nm pore diameter. If the temperature of the CVD process decreased to 550 °C, only CNTs were formed and there was no evident effect of boiling in water. When the CVD temperature decreased further to 500 °C, no CNTs or nanofibers were formed.

Lee *et al.* also described a CVD process with AAO templates to fabricate CNTs.¹³⁵ In their work, CNTs were synthesized through the decomposition of acetylene/argon at 800 °C for 20 min in the infrared tube furnace. In this case at first, a niobium layer of 200 nm thickness was deposited on an oxidized silicon wafer before AAO template formation. After aluminium was completely consumed, the niobium layer was anodized to create an oxide catalyst on the bottom of the template. Average pore diameter in the template was 70 nm. CNTs formed in the template had the same diameter as pores. If plasma treatment in oxygen for 10 min (100 W of RF power) is applied, the uniform length of the CNTs is obtained after dissolution of the template.

Chang *et al.* proposed a simple, inexpensive and reproducible method to produce nanoscale electrode arrays in large areas. They prepared vertically aligned MWNTs with a bamboo-like structure and high density on a large area of plain quartz substrates using PECVD. Ammonia and acetylene were used as the etchant gases and the carbon source, respectively. MWNTs were grown on a TiN coated quartz plate with Fe catalysts patterned by UV nanoimprint lithography (NIL). Patterned catalysts allow the precise placement of individual CNT electrodes on the substrate. The prepared electrodes had diameters ranging from 50 nm to 100 nm and lengths of about 300 nm. In addition, they investigated the biocompatibility by cell culturing on the fabricated CNTs/quartz template for potential bioapplications.¹³⁶

2.3.3 Liquid pyrolysis. The aerosol pyrolysis process is a catalytic CVD-based method involving pyrolysis of mixed liquid aerosols composed of both liquid hydrocarbon and catalyst precursor. Byeon and colleagues developed a new aerosol-assisted chemical vapour deposition (AACVD) process to synthesize vertically aligned CNTs arrays with outstanding height (4.38 mm) with very low metal contents in a short time (20 min) without supporting materials and water-assistance. An essential part of this technique was *in situ* formation of metal catalyst nanoparticles *via* pyrolysis of ferrocene-ethanol aerosol right before CNTs synthesis.¹³⁷

Jeong *et al.* presented an ultrasonic evaporator atomizing the mixed liquid solution for MWNTs production by the thermal pyrolysis process. They produced aligned and clean CNTs which can be easily controlled in a cost-effective manner.¹³⁸ A similar approach for nitrogen-doped CNTs with the tunable structure and high yield production by ultrasonic spray pyrolysis was done by Liu *et al.*¹³⁹ Khatri *et al.* reported SWNTs synthesis using ethanol and bimetallic catalyst of cobalt and molybdenum acetates by an ultrasonic spray pyrolysis method on silicon substrates at 850 °C.¹⁴⁰ Later, this author focused his research on zeolites powder as catalyst supporting material for SWNTs production using ultrasonic spray pyrolysis.¹⁴¹ In another study, Camarena and colleagues prepared MWNTs by spray pyrolysis using toluene as the carbon source and ferrocene as the catalyst.¹⁴² Sadeghian reported preparation of MWNTs by spray pyrolysis, using hexane as a carbon source and ferrocene as a catalyst precursor.¹⁴³ Clean and aligned MWNTs produced by aerosol pyrolysis of mixed liquid aerosols composed of both liquid hydrocarbon (toluene or cyclohexane) and catalyst precursor (ferrocene) were also reported by Pinault *et al.*¹⁴⁴ In another work, Nebol'sin and Vorob'ev studied CNTs growth *via*

catalytic pyrolysis of acetylene. They found that surface free energy plays a key role in determining the catalytic activity of the liquid droplet on the CNT tip and is responsible for the constant nanotube diameter.¹⁴⁵ An interesting paper describing the usage of a less common liquid carbon source, namely various pinene components isolated from turpentine, for MWNTs production by spray pyrolysis was recently published by Lara-Romero *et al.*¹⁴⁶ Next, a green natural carbon source for CNTs fabrication, neem oil extracted from the seeds of the neem-*Azadirachta indica*, was tested in the work of Kumar *et al.*¹⁴⁷ Similarly, coconut oil can be also used as a natural renewable precursor for MWNTs synthesis.¹⁴⁸

Quan *et al.* reported a new and interesting way of CNTs synthesis through waste pyrolysis oil. This process is based on treatment of waste pyrolysis liquid from printed circuit board (PCB) waste, which contains high concentrations of phenol and phenol derivatives. Hence, it can be applied as a carbon source in the preparation of advanced carbonaceous materials like CNTs. First, the pyrolysis oil is prepared by pyrolysis of PCB waste at 600 °C. In the second step, the product is polymerized in a formaldehyde solution to synthesize pyrolysis oil-based resin which is used as the precursor CNTs. Finally, this resin was mixed with ferrocene and homogenized in ethanol. After alcohol evaporation, the mixture was ground into fine powder, loaded on a ceramic boat and placed inside a stainless steel tubular reactor. The mixture was heated to 200 °C in air with 1 h soaking time, and then up to 900 °C in a flow of N₂ with holding periods for 1 h at 900 °C. The resulting CNTs had hollow cores with outer diameter of 338 nm and wall thickness of 86 nm and most of them were filled with metal nanoparticles or nanorods. X-Ray diffraction revealed that CNTs had an amorphous structure.¹⁴⁹

Ionescu *et al.* presented, that for a safe and easy way to scale up the CNTs growth, which is applicable in industrial production, it is possible to use spray pyrolysis CVD in the absence of hydrogen at low carrier gas flow rates and at relatively low synthesis temperature (typically 750 °C). They concluded that this approach promises great potential in building various nanodevices with different electron conducting requirements.¹⁵⁰

2.3.4 Solid state pyrolysis. Nowadays, solid state pyrolysis for CNTs synthesis is less frequently used compared to previously mentioned ones. Kucukayan and colleagues synthesized MWNTs through pyrolysis of the sulfuric acid-carbonized byproduct of sucrose. They observed the presence of sulfur in catalyst particles trapped inside nanotubes, but no sulfur was present in the side-walls of the CNTs.¹⁵¹ Clauss *et al.* thermally decomposed two nitrogen-rich iron salts, ferric ferrocyanide (Prussian Blue, "PB") and iron melonate ("FeM") in a microwave oven, which was used to heat a molybdenum wire after being coated with the precursor and protected from ambient atmosphere. While the PB-precursor did not give any nanotube-containing products, the FeM-precursor furnished tubular carbon nanostructures in a reproducible manner. This result may be due to the graphite-like nature of the melonate anions presented in FeM.¹⁵² Kuang *et al.* synthesized straight CNTs in large scale through thermal CVD by pyrolysis of two mixed metal phthalocyanines with a certain amount of S at 800–950 °C. The as-synthesized CNTs were 15–35 nm in diameter and 200–800 nm in length, quite straight and well-graphitized with nearly no

defects. Two kinds of mixed transition metal phthalocyanines (M(II)Pc, M = Fe, Co) were used as the carbon source as well as catalysts favoring the growth of the straight CNTs.¹⁵³ Du *et al.* prepared MWNTs through the solid-phase transformation of metal-containing glass-like carbon nanoparticles by heating at temperatures of 800–1000 °C. From microscopic observations on the morphologies and structures of the nanotubes and various intermediate objects, it is shown that the transformation occurs by nanoparticles first assembling into wire-like nanostructures, and then transforming into nanotubes *via* particle-particle coalescence and structural crystallization.¹⁵⁴ El Hamaoui studied the influence of novel polyphenylene-metal complexes to synthesis of various carbon nanoparticles (CNPs) including graphitic CNTs, graphitic carbon rods, and carbon-metal hybrid particles by solid-state pyrolysis of these complexes. The ultimate structures of the CNPs were found to depend on the structure and composition of the starting compounds. Precursors containing graphenes always result in graphitic CNTs in high yield, whereas dendritic precursors given rodlike carbon materials. Alternatively, linear oligo(arylethylene) precursors afford mostly carbon-metal hybrids with large amounts of amorphous carbon.¹⁵⁵

2.4 Flame pyrolysis

This technique is presented very uniquely by the research group of Liu *et al.* as a new method for mass CNTs production using simple equipment and experimental conditions. The authors called it V-type pyrolysis flame. They captured successfully CNTs with less impurities and high yield using carbon monoxide as the carbon source. Acetylene/air premixed gas provided heat by combustion. Pentacarbonyl was used as the catalyst and hydrogen/helium premixed gas acted as diluted and protection gas. The diameter of obtained CNTs was approximately between 10 nm and 20 nm, and its length was dozens of microns.¹⁵⁶ Moreover they studied the effect of sampling time, hydrogen and helium to the CNTs growth process.^{157–159}

2.5 Bottom-up organic approach

The bottom-up approach to integrate vertically PECVD grown MWNTs into multilevel interconnects in silicon integrated-circuit manufacturing from patterned catalyst spot was reported first by Li *et al.*¹⁶⁰

More recently, Jasti and Bertozzi described in their frontier article the potential advantages, recent advances, and challenges that lie ahead for the bottom-up organic synthesis of homogeneous CNTs with well-defined structures.¹⁶¹ Current synthetic methods used for CNTs fabrication produce mixtures of structures with varying physical properties. Jasti and Bertozzi demonstrated the CNTs synthesis with control of chirality, which relies on utilizing hoop-shaped carbon macrocycles, *i.e.* small fragments of CNTs that retain information regarding chirality and diameter, as templates for CNTs synthesis (Fig. 7). Their strategy lies in two basic areas: the synthesis of aromatic macrocyclic templates and the development of polymerization reactions to extend these templates into longer CNTs. This approach is particularly attractive because it can be used for synthesis of both zigzag and armchair CNTs of different

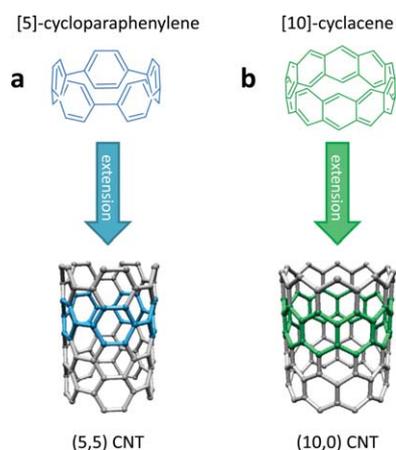


Fig. 7 Bottom-up, organic synthesis approach to CNTs with discrete chirality, modified according to ref. 161

diameters, as well as of chiral CNTs with various helical pitches. For example, a (5, 5) armchair CNT can be constructed by fusing additional phenyl rings to [5]cycloparaphenylene (Fig. 7a). In similar fashion, a (10, 0) zigzag CNT can be constructed from [10]cyclacene (Fig. 7b).

Since the publication work of Jasti and Bertozzi, several approaches for carbon macrocycles as a step toward the bottom-up synthesis of CNTs with selective chirality have been reported. Omachi *et al.* reported a modular and size-selective synthesis of [14]-, [15]-, and [16]cycloparaphenylenes for selective synthesis of [n,n] type SWNTs.¹⁶² Concise synthesis of [12]cycloparaphenylene and its crystal structure was presented by Segawa *et al.*¹⁶³ A simple and realistic model for the shortest sidewall segments of chiral SWNTs has been designed, and one of the chiral carbon nanorings, cyclo[13]paraphenylene-2,6-naphthylene for chemical synthesis of chiral CNTs has been successfully synthesized by Omachi *et al.*¹⁶⁴ Selective and random synthesis of a [8]–[13] cycloparaphenylenes mixture was prepared in good combined yields by mixing biphenyl and terphenyl precursors with platinum sources by Iwamoto *et al.*¹⁶⁵ Finally Fort and Scott also presented interesting groundwork for the selective solvent-free growth of uniform diameter armchair CNTs by gas-phase Diels–Alder cycloaddition of benzyne to an aromatic hydrocarbon bay region on the rims of suitable cylindrical hydrocarbon templates followed by rearomatizations and thermal cyclodehydrogenations to join adjacent benzo groups.¹⁶⁶

3. Conclusions

Although the growth mechanism of CNTs is not exactly known, new synthesis methods for higher yield, higher purity and low defects of produced CNTs are main points of investigation which are pushed forward by the prospering fields of nanotechnology and nanoscience that have many ideas of possible applications. In this paper, we reviewed the history, types, structures and especially the different synthesis methods for CNTs preparation including arc discharge, laser ablation and CVD and some new approaches of synthesis regarding the various CNTs types, namely MWNTs, SWNTs and DWNTs. The problem of purification of CNTs has been discussed as well.

Special emphasis is given to CVD and PECVD techniques as the most utilized methods in the last few years. Moreover, we mentioned some rarely used ways of arc discharge deposition which involve arc discharge in liquid solutions contrary to the standard use of deposition in a gas atmosphere. In addition, the methods for uniform vertically aligned CNTs synthesis using lithographic techniques for catalyst deposition as well as a method utilizing a nanoporous anodized aluminium oxide as a pattern for selective CNTs grown are reported too.

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