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Chapter 6

CHEMICAL VAPOR DEPOSITIONS FOR CARBON NANOTUBES SYNTHESIS

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ABSTRACT

Carbon nanotubes (CNTs) have been under scientific investigation more than fifteen years since their unique properties predestine them for numerous 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 chapter, brief history, types, structure and especially the different synthesis methods for CNTs preparation are reviewed. The attention is mainly aimed on various types of chemical vapor depositions as CVD methods for uniform vertically aligned CNT synthesis, liquid pyrolysis and solid state pyrolysis.

INTRODUCTION

Recently, the investigation of nanoparticles is one of high-profile challenges in scientific word. Many scientific papers have been already published about the preparation of different nanoparticles. Nano-allotropes of carbon including fullerenes (Figure 1a), graphene (Figure

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1b) and carbon nanotubes (Figure 1c,d) represent one group of the most promising materials due to their unique electrical, optical, mechanical, thermal, chemical and other properties which predestine them for use in many applications, such as electronic chips, conductive films, supercapacitors, fuel cells, memories, displays, filters, solar cells, sensors, clothes, etc.

The discovery of buckminsterfullerene (C_{60}) (Figure 1a) in 1985 by Kroto et al. led to an entirely new branch of carbon chemistry [1]. In the early 1990s, another significant breakthrough was achieved. Carbon filaments with diameters within the nanometer range were observed by Iijima using transmission electron microscopy (TEM) [2]. These carbon filaments were called carbon nanotubes (CNTs). Two years later, single-walled carbon nanotubes (SWCNTs) were synthesized by Iijima and Ichihashi [3] and Bethune et al. [4]. Vertically-aligned carbon nanotubes (VACNTs) were first reported by Thess et al. [5] who were able to bundle 70% of the volume of nanotubes into crystalline ropes in 1996. In the same year, the Chinese Academy of Science reported that a 50 μm -thick film of highly aligned nanotubes had successfully been grown by chemical vapor deposition (CVD) [6]. Ren and Huang [7] first used Plasma-Enhanced Hot Filament CVD (PE-HF-CVD) to lower the growth temperature below 666 $^{\circ}\text{C}$ and they used electric field as an external force to provoke the alignment. Meanwhile, Fan et al. [8] introduced position controlled growth of VACNTs on porous and plain silicon substrate. They also reported the detailed growth and mechanism of alignment of ACNTs in their work. Since these great discoveries, this topic has been reviewed numerous times [9-11]. The aim of this study is to provide a short review about the current methods used for CNTs synthesis.

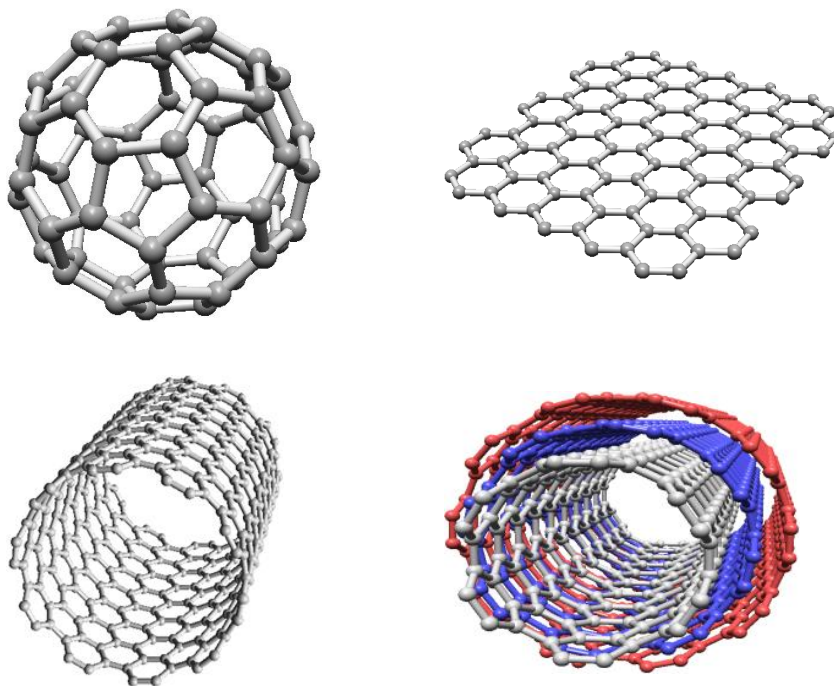


Figure 1 Nano-allotropes of carbon. A) fullerene C_{60} ; B) graphene sheet; C) single-walled carbon nanotube; D) multiwalled carbon nanotube.

First method used for CNTs fabrication by Iijima in 1991 was arc discharge [2] where the growth process is held between two graphite - usually water-cooled -electrodes at high temperatures (above 1700°C). It is performed in a chamber filled with helium at subatmospheric pressure which usually causes the growth of CNTs with fewer structural defects in comparison with other techniques. Another method especially used for high purity SWCNTs is laser ablation utilizing Nd:YAG and CO₂ lasers where the laser energy is used for graphite target evaporation.

Nowadays, these two methods were replaced by low temperature chemical vapor deposition (CVD) techniques, because the orientation, growth over masked areas, alignment, nanotube length, diameter, purity and density of CNTs can be precisely controlled. In this approach, a feedstock such as CO or a hydrocarbon is heated to 800–1000°C with a transition metal catalyst to promote nanotube growth [12]. In general, CVD is a chemical process used to produce high-purity, high-performance solid materials. Catalytic chemical vapor deposition (CCVD) – either thermal [13] 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 [14-16], oxygen-assisted CVD [17], hot-filament (HFCVD) [18, 19], microwave plasma (MPECVD) [20, 21] or radiofrequency CVD (RF-CVD) [22]. CCVD is considered to be the 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, high purity of the obtained material, etc. [23].

CNT growth model is still under discussion. Recently, Fotopoulos and Xanthakis discussed the traditionally accepted models - 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 advert to a 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 [24]. In order to produce SWNTs, the size of the nanoparticle catalyst must be smaller than about 3 nm.

The function of the catalyst in 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 [25]. Sometimes, the traditionally used catalysts are further doped with other metals, e.g. with Au [26]. Concerning the carbon source, the most preferred in CVD are hydrocarbons such as methane [27], ethane [28], ethylene [29], acetylene [30], xylene [31, 32], eventually their mixture [33], isobutane [34], and ethanol [35, 36]. In case of gaseous carbon source, the CNTs growth efficiency strongly depends on the reactivity and concentration of gas phase intermediates; these are produced together with reactive species and free radicals as a result of hydrocarbon decomposition. Thus, it can be expected that the most efficient intermediates with potential of chemisorption or physisorption on the catalyst surface to initiate CNT growth should be produced in the gas phase [37].

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 [38] [39]. 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 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 [40]. Similarly, Ramesh et al. succeeded in high-yield selective CVD synthesis of DWNTs over Fe/Co loaded high-temperature stable mesoporous silica [41]. 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 the selective synthesis of DWNTs [42].

The choice of catalyst is one of the most important parameters affecting the CNTs growth. Therefore, its preparation represents 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 the review of Szabo et al. [43]. 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 milder combustion conditions obtained in 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 [44]. 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 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 [45].

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 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 [46]. Zhang et al. prepared MWNTs with diameter 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 [47, 48]. Sano and colleagues evaluated two systems of metallic catalyst/carbon source for CNTs growth: ethanol/Co and benzene/Fe. Moreover, they investigated two different reactors (gas-flow reactor and a submerged-in-liquid reactor) effect on quality of CNTs [49]. Jiang et al. studied the grow of CNTs in situ on the pre-treated graphite electrode (GE) via CCVD using Ni(NO₃)₂ as the catalyst [50]. The prepared CNTs had 80 and 20 nm in outer and inner diameters, respectively. Moreover, the CNTs were not very long (comparing with data reported elsewhere): their length was from 200 to 1000 nm as a result of shorter growing time. Scheibe et al. tested Fe and Co for MWNTs fabrication. Additionally, these authors were interested in the concentration of the carboxyl and hydroxyl groups on the carbon nanotube surface because both are essential features for applications in many science branches such as nanomedicine, biosensors or polymer nanocomposites [51].

Feng et al. used acetone as a carbon source, ferrocene as a source of Fe catalyst and thiophene as a promoter to synthesize high-quality DWNTs thin-films in one-step CCVD reaction process in an argon flow [52]. Li studied the synthesis of well aligned MWNTs on large area Ni-deposited SiO₂/Si substrates via the pyrolysis of C₂H₂ using thermal CVD technique at 900 °C. He found that NH₃ pre-treatment was crucial to control the surface morphology of catalytic metals and thus to achieve the vertical alignment of CNTs. With higher density of Ni particles, better alignment of the CNTs can be obtained due to steric hindrance effect between neighboring CNTs. The degree of crystallization of the CNTs

increased with increasing NH_3 pre-treatment time. Energy dispersive X-ray spectrum analysis revealed that CNTs grew by a tip growth mechanism [53]. 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 [54].

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 were 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 [55].

Cui et al. synthesized thin-walled, open-ended, 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 increases while the Fe encapsulation in CNTs decreases as the growth temperature rises in the range of 780–860 °C [56].

Grazhulene et al. prepared CNTs by CCVD using ethanol vapor 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. HNO_3 in an autoclave at 110–120 °C possessed the maximum adsorption capacity of all studied elements. It 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 [57].

Du et al. synthesized CNTs by Co/MgO catalyzed pyrolysis of dimethyl sulphide ($\text{C}_2\text{H}_6\text{S}$) at 1000 °C which is rarely used as a carbon source. The presence of sulphur can promote the growth of long SWNTs or branched CNTs (BNTs). They found that $\text{C}_2\text{H}_6\text{S}$ vapor 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 a high flow rate of $\text{C}_2\text{H}_6\text{S}$ vapor [58].

PECVD

Plasma-enhanced chemical vapor deposition (PECVD) is a suitable method for the synthesis of CNTs hybrid materials and modification of their surface properties. PECVD is

also used for its ability to produce VACNTs. Lim et al. reviewed the application of PECVD in the production and modification of CNTs. They emphasize the use of PECVD method for SWNTs growing at low temperatures and make an effort to better understanding plasma chemistry and modeling [59]. An example of MWNTs forest-like structure deposited on solid substrate using PECVD is shown in Figure 2. PECVD can be also used in several different modes: radio frequency (RF-PECVD), direct current (DC-PECVD), diffusion (DPECVD) or microwave (MWPECVD). Kim et al. 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 Fe/Al bilayer as catalyst [60]. 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 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 [61].

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 $\text{Ni}(\text{NO}_3)_2$ 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 the synthesis of vertically-aligned CNTs by PECVD in an electron cyclotron resonance chamber using a gas mixture of $\text{C}_2\text{H}_2/\text{NH}_3$ at 520 °C. The average thickness of the CNTs film was about 1 μm and the CNTs diameter was around 50 nm.

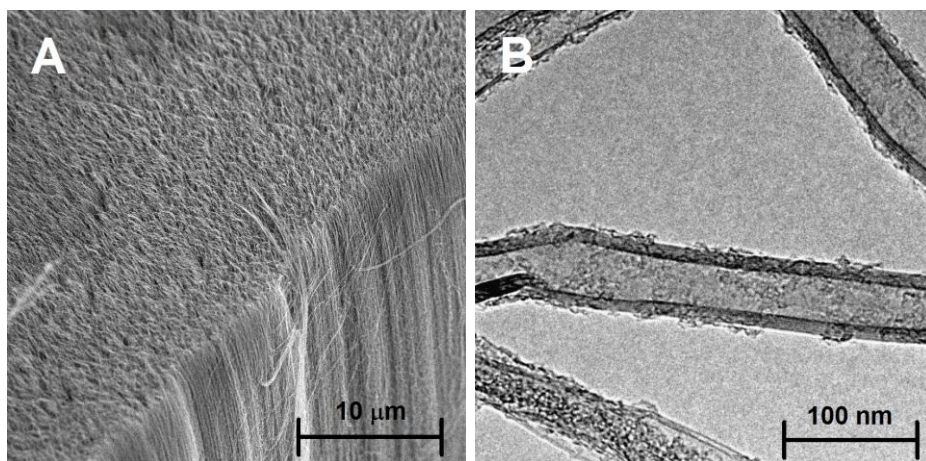


Figure 2. MWNTs forest-like structure deposited using CVD. A) SEM image; B) TEM image.

After CNTs preparation, their surface was functionalized with oxygenated and aminated groups using microwave plasma to make them suitable for a future biosensing application. Moreover, they found that the plasma treatment was a very effective way to retain the CNTs aligned forest structure of electrode surface [62]. He et al. focused their study on a TEM investigation of the crystallography of Ni catalysts for the vertical growth of carbon

nanofibers (CNFs), synthesized by DC PECVD in an atmosphere composed of isopropyl alcohol and water [63, 64]. Yung and colleagues tested the influence of four types of substrates, namely Si, n++ Si, p++ Si, and SiO₂, on CNTs growth on Ni catalyst layer using PECVD. They found that the type of Si substrate has significant effects on CNT growing characteristics [65]. 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 that 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 [66].

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 nanometers 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 the 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) [67]. 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): PECVD at 450 °C to 500 °C and atmospheric-pressure chemical vapor 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 [68]. Another method for the synthesis of CNTs using an atmospheric-pressure microwave (MW) torch was presented by Zajickova et al. [69, 70]. The apparatus shown in Figure 3 was successfully applied in the fast deposition of multiwalled nanotubes (MWNTs) on a substrate without the necessity of any vacuum or heating equipment. Dense straight-standing nanotubes were prepared on Si substrates with and also without barrier Si Ox layer. Therefore, it was possible to produce CNTs directly on conductive Si and to use them as an electron-emitting electrode of the gas pressure sensor. The CNTs grown in MW torch were also used to create a gas sensor based on the changes of electrical resistance measured between two planar electrodes connected by the CNTs.

However, some works were published with no use of catalysts for CNTs growing. Qu and colleagues prepared new hybrid material consisting of spontaneous assembly of carbon nanospheres on aligned or non-aligned SWNTs using 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 [71].

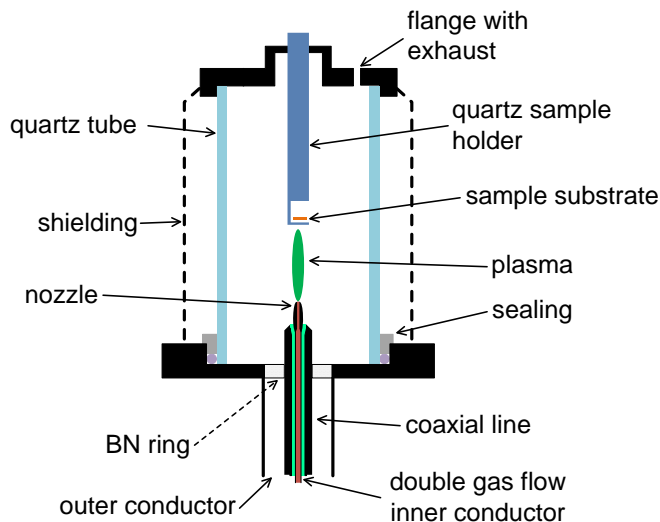


Figure 3. Set-up of the apparatus for atmospheric-pressure MW PECVD MWCNTs direct deposition (modified according to [69]).

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 the diameter of about 30 nm and the 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 [72].

Jang and colleagues fabricated flexible thin film transistors (TFT) with randomly oriented single-walled SWNTs synthesized selectively on a designed array of catalyst photoresists using PECVD method. The process involves SWNTs growth on SiO_2/Si substrates. This might be of interest for various applications of SWNTs in flexible electronics [73]. Ono et al. also prepared TFT with a carbon CNTs network as a channel using grid-inserted PECVD [74]. Yung et al. synthesized two types of hybrid carbon materials by RF-PECVD: the tree-CNTs with branches of different diameter using ferrocene powder as a catalyst and the wing-like CNTs with graphitic-sheets of different density using Co or Ni thin film coated on the surface of Ti thin film (20 nm). In both cases, Si(100) was used as a 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. It can be ascribed to the effects of branch size, crystal orientation, and graphitic-sheet density [75]. 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 pre-treated using H_2 plasma at 600 $^\circ\text{C}$ for 3 min and the CNTs grew with the different thickness of catalyst layer for 30 min at 600 $^\circ\text{C}$ [76]. 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 $^\circ\text{C}$. They functionalized the CNTs surface with 1H,1H-2H,2H 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 [77]. 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 [78].

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 [79]. The aim of several works was to fabricate vertically-aligned CNTs with homogenous distribution on the surfaces and high uniformity. It is evident that one may be able to create patterns of catalyst on the surface on which CNTs are formed using CVD methods using nanolithography. Kim et al. used Si wafer as substrate and Ni as catalyst deposited on 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 used the triode PECVD reactor with gas ratio $\text{C}_2\text{H}_2/(\text{H}_2 \text{ or } \text{NH}_3)$ 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 [80]. Yamada et al. used high efficiency water-assisted CVD synthesis of vertically-aligned DWNTs forests with heights of up to 2.2 μm with Fe as a catalyst. CNTs with a carbon purity of 99.95 % were achieved [81].

Very interesting methods are those using non-lithographic techniques. The most frequently employed method of aligned CNTs formation is the usage of nanoporous anodized aluminium oxide (AAO) as template for CNTs growth. In the work of Kim et al. [82], the CNTs were grown on a 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 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 were 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 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 with thermal CVD because CNTs were not grown on the AAO/Si barrier. Graphitization of the CNTs was very poor as compared to the CNTs grown on glass substrate using thermal CVD. The CNTs grown on the barrier between pores does not look like a nanotube but a carbon nanofiber. In the case of Type B, the length of CNT is almost the same as the pore depth because CNTs did not grow on AAO/Si barrier, but only on the catalyst on the bottom of the pores. CNTs grew on AAO/Si without the catalyst, while there was no overgrowth of CNTs on AAO/Si with a catalyst. In the synthesis of CNTs using AAO template with/without Co layer, both alumina and Co can work as catalysts with flowing acetylene.

Similar work employing CVD on AAO template was reported by Sui et al. [83]. The authors found that the pores in templates had diameters of 24 nm and 86 nm according to anodizing voltage and acid employed. 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 N_2/C_2H_2 (90:10) with a rate of 100 ml/min 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 appearance 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 CVD process decreased to 550 °C, only CNTs were formed and there was no evident effect of previous boiling in water. When the CVD temperature decreased further to 500 °C, no CNTs or nanofibers were formed.

Lee et al. also described CVD process with AAO templates to fabricate CNTs [84]. 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 thick was deposited on an oxidized silicon wafer before the AAO template formation. After aluminium was completely consumed, the niobium layer was anodized to create 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) was applied, the uniform length of the CNTs was 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 allowed 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, the biocompatibility by cell culturing on the fabricated CNTs/quartz template for potential bioapplications was investigated [85].

LIQUID PYROLYSIS

Aerosol pyrolysis process is a catalytic CVD-based method involving pyrolysis of mixed liquid aerosols composed of both liquid hydrocarbon and a catalyst precursor. Byeon and colleagues developed a new aerosol-assisted chemical vapor deposition (AACVD) process to synthesize vertically-aligned CNTs arrays with outstanding height (4.38 mm) with very low metal contents in short time (20 min) without supporting materials and water-assistance. An essential part of this technique is in-situ formation of metal catalyst nanoparticles via pyrolysis of ferrocene-ethanol aerosol right before CNTs synthesis [86].

Jeong et al. presented 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 [87]. A similar approach for nitrogen-doped CNTs with tuneable structure and high yield production by ultrasonic spray pyrolysis was done by Liu et al. [88]. Khatri et al. reported SWNTs synthesis using ethanol and bimetallic catalyst of cobalt and molybdenum acetates by ultrasonic spray pyrolysis method on silicon substrates at 850 °C [89]. Later, these authors focused their research on zeolites powder as catalyst supporting material for SWNTs production using ultrasonic spray pyrolysis [90]. In another study, Camarena and colleagues prepared MWNTs by spray pyrolysis using toluene as carbon source and ferrocene as catalyst [91]. Sadeghian reported preparation of MWNTs by spray pyrolysis, using hexane as a carbon source and ferrocene as a catalyst precursor [92]. 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. [93]. In another work, Nebol'sin et al. 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 [94]. An interesting paper describing a usage of 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. [95]. Further, the green natural carbon source for CNTs fabrication, neem oil extracted from the seeds of the neem-*Azadirachta indica*, was tested in the study of Kumar et al. [96]. Similarly, coconut oil can be also used as a natural renewable precursor for MWNTs synthesis [97].

Quan et al. reported the 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. Primarily the pyrolysis oil is prepared by pyrolysis of PCB waste at 600 °C. In the second step, the product is polymerized in formaldehyde solution to synthesize pyrolysis oil-based resin which is used as a precursor of 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 [98].

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 temperatures (typically 750 °C). They concluded that this approach promises great potential in building various nanodevices with different electron conducting requirements [99].

SOLID STATE PYROLYSIS

Nowadays, solid state pyrolysis for CNTs synthesis is less frequently used compared to those previously mentioned. Kucukayan and colleagues synthesized MWNTs through pyrolysis of the sulfuric acid-carbonized by-product of sucrose. They observed that the presence of sulfur in catalyst particles trapped inside nanotubes, but no sulphur was presented in the side-walls of the CNTs [100]. Clauss et al. thermally decomposed two nitrogen-rich iron salts, ferric ferrocyanide (Prussian Blue, "PB") and iron melonate ("FeM"), in a microwave oven. It 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 [101]. 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 carbon source as well as catalysts favoring the growth of the straight CNTs [102]. 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 [103]. El Hamaoui studied the influence of novel polyphenylene-metal complexes onto 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 rod-like carbon materials. Alternatively, linear oligo (arylethylene) precursors afford mostly carbon-metal hybrids with large amounts of amorphous carbon [104].

CONCLUSION

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. This research is pushed forward by the prospering fields of nanotechnology and nanoscience that have many ideas of possible applications. In this paper, the history, types, structure and especially the CVD and PECVD techniques of CNTs synthesis are briefly reviewed. These two methods are the most utilized ones in the last few years and some new approaches of CVD synthesis regarding the various CNTs types, namely MWNTs, SWNTs and DWNTs are reported. 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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