

Chapter

Synthesis of Carbon Nanotubes by Catalytic Chemical Vapor Deposition

Xiao-Di Wang, K. Vinodgopal and Gui-Ping Dai

Abstract

As a new carbon material in the twenty-first century, carbon nanotubes (CNTs) have excellent optical, electrical, magnetic, thermal, chemical, and mechanical properties. There are many synthesis methods to produce CNTs. Compared with other methods, chemical vapor deposition (CVD) is the most effective method that has broad prospects for large-scale control of CNTs in recent years due to its simple equipment, simple operation, and lower cost. In order to gain a comprehensive understanding of the controlling parameters about the formation of CNTs, this chapter reviews the latest progress in the preparation of CNTs by CVD from three of the most important influencing factors: carbon sources, catalysts, and substrates. Among them, the catalyst is the most influential factor for the morphology, structure, and properties of CNTs. It should be pointed out that many growth factors can control the particle size distribution, composition, and structure of the catalysts, such as catalyst substrate, metal transition components added, calcination temperature, etc.

Keywords: synthesis, CVD, carbon nanotubes

1. Introduction

In order to meet the challenge of the increase of global energy consumption and the augment of global financial markets and population in the past time, people have opened up new fields in materials science such as nanotechnology. Carbon-based nanomaterials have caused great concern in the light of their unique structure and extraordinary physical properties (**Table 1**).

Generally speaking, carbon is mainly retained as solid carbon including graphite and diamond. With the rapid development of science and technology, more and more carbon nanostructured materials are discovered. In 1975, Oberlin et al. [1] successfully prepared carbon nanofibers by CVD, which has aroused the upsurge in the research of carbon nanomaterials. In 1985, fullerene [2], a zero-dimensional carbon nanomaterial, was discovered. Later, Iijima [3] accidentally discovered what is now known as the CNT needle (**Figure 1**) when he used TEM to observe the products by the arc discharge process. The investigation of CNTs was heating up since their discovery. The preparation and application of CNTs are one of the examples for the current industry technology. In 2004, Geim and Novoselov [4] mechanically peeled off the graphite repeatedly until it formed a plane of a single atom and found another allotrope of carbon named graphene.

Properties		SWCNTs	MWCNTs	Comparison
Mechanical properties	Young's modulus	~1 TPa	~1–1.2 TPa	About 5 times stronger than steel
	Tensile strength	~60 GPa	~0.15 TPa	About 100 times stronger than steel
Electronic properties	Bandgap	When n-m is divisible by 3 (0 eV, metallic) When n-m is not divisible by 3 (0.4–2 eV, semiconducting)	~ 0 eV (non-semiconducting)	
Thermal properties	Thermal conductivity at room temperature	1750–5800 W/mk	>3000 W/mk	About 3 times better than diamond
Electrical properties	Typical resistivity	$10^{-6} \Omega \text{ m}$		
	Typical maximum current density	$10^7\text{--}10^9 \text{ A cm}^{-2}$		
	Typical quantized conductance (measured)	$12.9 \text{ k}\Omega^{-1}$		

Table 1.
Some excellent properties of CNTs.

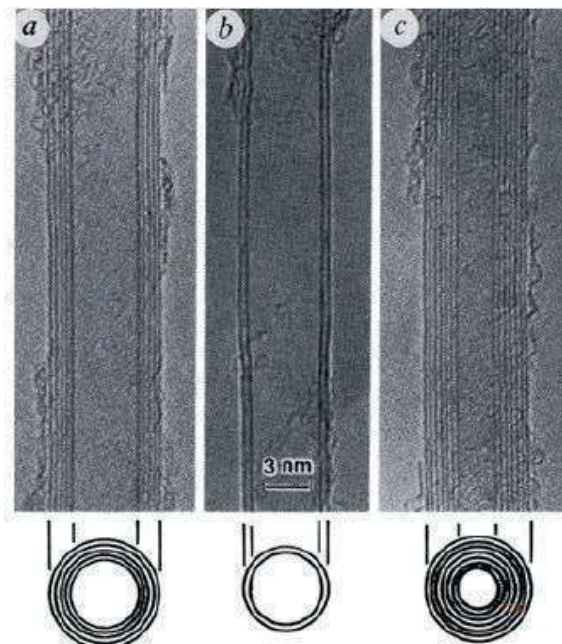


Figure 1.
CNTs firstly discovered by Iijima in 1991. Reproduced with permission of Ref. [3].

CNTs are tubes that are rolled up by a layer or several layers of graphite, or that can be coaxially wrapped together by different diameters of microtubules, which have only a few nanometers in diameter. The spacing between the tube walls is about the size of graphite layer spacing. There are two ways of hybridizing carbon

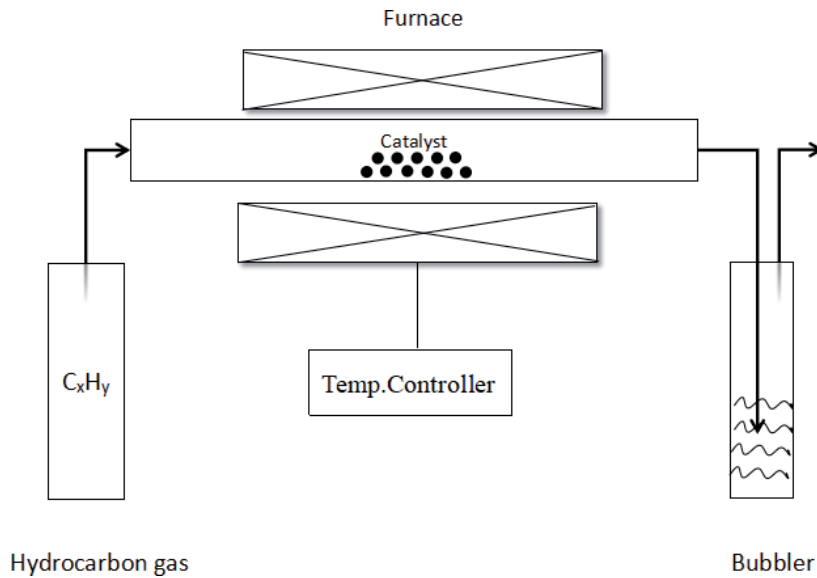


Figure 2.
Simple form of CVD setup.

atoms in CNTs, mainly sp^2 hybridization, and specific sp^3 bonds can also be formed between hexagonal carbon atoms.

CNTs are classified as single-walled CNTs and multi-wall CNTs according to the layer number of graphene sheets. Because there is only one layer of graphene in SWCNTs, the diameter range of SWCNTs is smaller than that of MWCNTs, which is only 0.4–3 nm. Therefore, the application of single-walled CNTs in nanomaterials field is more promising. Multi-walled CNTs have graphene layers ranging from 2 and more. SWCNTs were firstly discovered by Iijima and Ichihashi [5] in 1993, CNTs formed by the coaxial crimping of two or more layers of graphene are called MWCNTs [3]. Besides, SWCNTs can be classified into three types according to their structural characteristics (depending on graphene sheet in a rolled manner as shown in **Figure 2**): armchair form, zigzag form, and chiral form. This difference is due to the fact that in the case of single-walled CNTs, the graphene sheets can be curled at any angle and therefore have different chiral structures. The chirality index of CNTs is directly related to the helicity and electrical properties of CNTs.

In addition to above, there is another fibrous carbon nanostructure which is rolled by multi-layer graphene called carbon nanofibers. Carbon nanofibers, which are fibrous carbon nanomaterials made from multilayer graphene sheets, are generally 10–500 nm in diameter and 0.5–100 nm in length, with high orientation, conductivity, and thermal conductivity.

CNTs are characterized by high mechanical strength, high specific surface, high conductivity and strong interfacial effect. They are widely used in energy storage devices, electrode materials, field emission displays, semiconductor materials, catalyst carriers, composite reinforcement, etc. The scale of all these applications mainly depends on quality, output, and cost of CNTs.

CNTs are strictly studied by scientists and engineers because of their special properties. The range of applications of CNTs covers almost every field of materials science; a wide variety of applications have also been widely reported such as electromagnetic and microwave absorbing coatings, sensors, radiation sources, and nanometer-sized semiconductor devices and thermal interface materials. CNT arrays can provide good thermal interface conductance for ionic and electronic transport devices such as batteries [6]. Dalton et al. [7] discovered that the low density, high aspect ratio, and extraordinary mechanical properties of CNTs make fibers super-tough particularly.

Method	Chemical vapor deposition	Arc discharge	Laser ablation
Condition	Low pressure inter gas (argon)	Argon or nitrogen gas at 500 Torr	High temperatures about 500–1000 °C at high energy laser beam
Yield	High (60–90%)	Low (20–100%)	Low (up to 70%)
Purity	Medium to high	Medium	Low
Temperature	500–1200°C	~4000°C	25–1000°C
Product	SWCNTs: long tubes with diameters ranging from 0.6 to 4 nm	SWCNTs: short tubes with diameters of 0.6–1.4 nm	SWCNTs: long bundles of tubes (5–20 μm) with individual diameter from 1 to 2 nm
	MWCNTs: long tubes with diameter ranging from 10 to 240 nm	MWCNTs: short tubes with inner diameter of 1–3 nm and outer diameter of approximately 10 nm	MWCNTs: not very much interest in this technique

Table 2. Comprehensive comparison of CVD and other preparation methods.

Directional carbon nanotube arrays can be used in photonic crystals, optical antennas, optical waveguides, solar cells, and so on [8–12]. Carbon nanotube arrays used in optoelectronic devices are three-dimensional ordered structure and are usually fabricated by PECVD. Carbon nanotubes are considered to be one of the best electron-emitting materials because of their high aspect ratio, which induces very high local electric fields at the top of carbon nanotubes [13]. The field emission characteristics of vertically oriented CNTs can be used in flat panel displays, high-strength electron sources, X-ray generators, and microwave devices [14–16].

If CNTs cannot be achieved as desired scale and controllable parameters according to the pre-designed structural model, all valuable applications disappear. Therefore, it is one of the key technologies for the development of CNTs with specific characteristics such as height, diameter, aspect ratio, morphology, large area, and scale preparation.

There are three most common preparation methods (**Table 2**) for CNTs: chemical vapor deposition, arc discharge, and laser ablation [6]. Among them, CVD is the most widely used method because of the continuous mass production and low cost.

Despite tremendous advances in carbon nanotube research in the past years, we have been unable to mass produce well-performing CNTs with cost-effective technologies. This chapter focused on chemical vapor deposition of CNTs. In terms of reaction materials, we discussed three aspects in detail: carbon source, catalyst and substrate, and growth process in CNTs. For growth parameters, we mainly discussed the effects of temperature on the morphology and properties of CNTs. In industrial production, we emphasized high yield, large yield, and high purity. Finally, we look forward to the future prospects of CNTs.

2. Chemical vapor deposition

It is important that large quality and high purity CNTs require highly reliable synthesis techniques. Understanding the influencing factors and control conditions of specific carbon nanotube synthesis is what we need.

At present, the preparation process of multi-walled CNTs is quite mature, and industrial production has been realized by the CVD. The production cost of

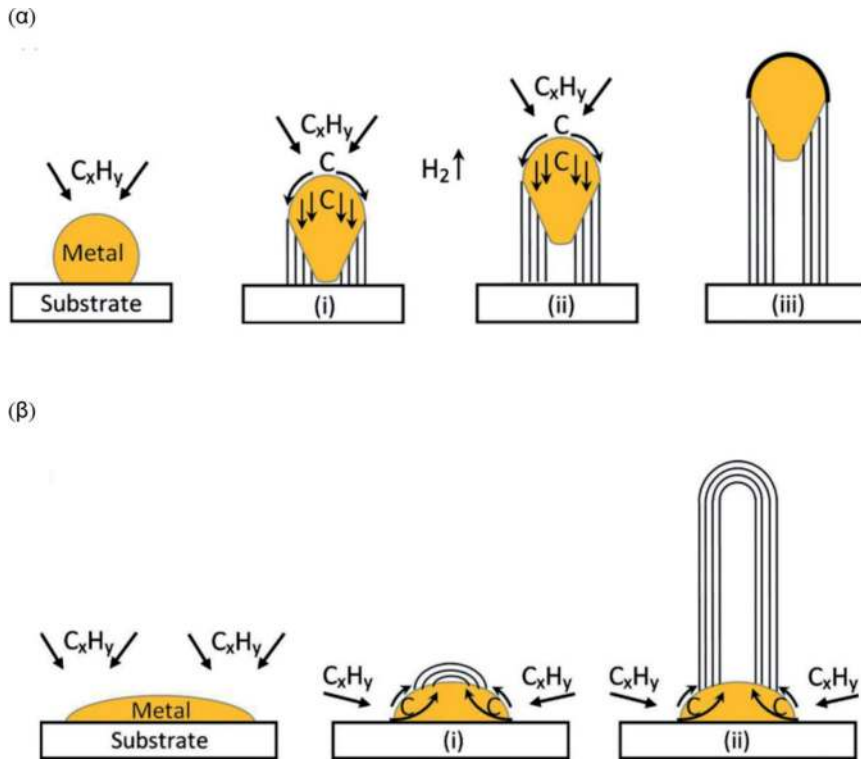


Figure 3. Two growth model diagrams for CNTs: (α) tip-growth mechanism and (β) root-growth mechanism. Reproduced with permission of Ref. [21].

single-walled CNTs is still quite high, and the preparation of macroscopic arrays of some oriented single-walled CNTs has not been realized.

The chemical vapor deposition method is to cleave a carbon atom-containing gas continuously flowing through the catalyst nanoparticle to generate carbon atoms and then generate CNTs on the surface of the catalyst or the substrate. The synthesis process is to let catalyst decompose carbon source (usually hydrocarbon gas) at a sufficiently high temperature in a tubular reactor [6]. **Figure 3** is a schematic diagram of the most common carbon nanotube production process by CVD.

The history of chemical vapor deposition can be traced back to the nineteenth century. In 1890, French scientists observed carbon filaments in experiments in which cyanobacteria spread on hot porcelain [17]. This material was formed by the interaction of carbon-containing gases with the surface of molten iron, which was first reported in 1896, but its structural details and mechanical properties are the result of recent advances in electron microscopy. CVD may be the first in the name of filaments and fiber-planted CNTs. But in 1996, CVD became a method of mass production and synthesis of CNTs [18].

Compared to other two methods, in terms of crystallinity, although the crystallinity of CVD-grown MWCNTs is low, the crystallinity of CVD-grown SWCNTs is close to that by arc or laser. However, CVD is superior to arc and laser methods in terms of yield and purity. CVD is the only viable method for structural control or growth parameter control.

Although the growth mechanism of CNTs has been controversial, there are currently two widely accepted mechanisms, and they can be summarized as follows. When a hydrocarbon vapor is contacted with heated metal nanoparticles, it is first decomposed into carbon and hydrogen. Hydrogen leaves with the passing carrier gas or reducing gas, and carbon dissolves in the metal catalyst. When the temperature

reaches the carbon solubility limit of the metal, the decomposed carbon particles precipitate and crystallize to form CNTs. The decomposition of hydrocarbons is an exothermic process, carbon crystallization is an endothermic process, and the thermal gradient continues this process. The reason for the two growth mechanisms is that the interaction between the catalyst and the substrate is different:

1. When the catalyst interacts weakly with the substrate, carbon decomposed from the hydrocarbon diffuses from the metal catalyst to the bottom of the metal catalyst and precipitates between the substrate and the metal catalyst, thereby promoting the growth of the entire metal catalyst nanoparticles. When the metal particle is entirely covered by excess carbon, growth stops, which is called tip-growth [19].
2. When the catalyst interacts strongly with the substrate, the carbon precipitates without pushing up the metal particles, so it is forced to precipitate from the top of the metal, which is called the “basic growth model,” also called root growth. [20]

During the synthesis of CNTs, many parameters affect the final morphology and properties of CNTs, such as carbon source, catalyst, reactor temperature, system pressure, flow rate of carrier gas, deposition time, reactor type, the geometry of reactor, catalyst support, active metal components in catalyst, and so on.

3. Carbon source

Precursors in CVD can be of any state, whether solid, liquid or gas. In the case of a liquid carbon source, it is only necessary to heat the liquid to become steam, and then enter the tubular reactor along with the inert gas or the reducing gas. If a solid hydrocarbon is used as the carbon source, it can be stored directly in the quartz boat together with the catalyst and placed together in the tubular reactor. In the case of volatile materials (camphor, naphthalene, etc.), they can be converted directly from solids to steam and then reacted on the catalyst as the gas enters the high temperature zone.

Also, molecular structure of the carbon source, air pressure, and so on have a great impact on the formation of CNT morphology.

In addition, the concentration of carbon source gas has also an impact on the mentality of CNTs. If the concentration is too high, too many CNTs can be wrapped by amorphous carbon and carbon nanoparticles, resulting in rough product surface [22]. This is mainly due to the excessive supply of carbon during the growth process. Therefore, proper control of carbon source gas concentration can effectively reduce or even remove excess substances on the CNT surface. Secondly, the purity of gas can also affect the generation of CNTs, as reported [23]. The oxygen content can significantly change the growth kinetics of CNTs.

The most common carbon sources are carbon monoxide, ethane, ethylene, acetylene, benzene, and xylene [21].

If the carbon source is a linear hydrocarbon such as methane, ethylene or acetylene, they are generally decomposed into linear dimers of carbon atoms or carbon at high temperatures, and synthesis by CVD can produce straight carbon nanotubes, and if it is benzene, two cyclic hydrocarbons such as toluene, fullerene, and cyclohexene can produce relatively curved carbon nanotubes [24, 25].

SWCNTs had higher formation energy than MWCNTs because SWCNTs have the characteristics of small diameter, large curvature, and high strain energy. This

is why most MWCNTs grow more easily than SWCNTs. In fact, MWCNTs is easily generated in a low temperature of 600–900°C, and usually at a higher temperature of 900–1200°C SWCNTs can be generated. SWCNTs must be grown from certain hydrocarbons, such as methane and carbon monoxide that maintain thermal stability at high temperatures. In contrast, the effective carbon sources for the synthesis of MWCNTs cannot be stable at high temperature, which can lead to a large amount of amorphous carbon impurities deposited outside the required products.

José-Yacamán et al. [26] produced helical MWCNTs at 700°C on iron nanoparticles as a catalyst using acetylene by the CVD method. And in an early research, Endo et al. [27] also developed MWCNTs using the same catalyst by the CVD method, except that the carbon source was changed to benzene, and the reaction temperature rose to 1100°C. Subsequently, cyclohexane [28] and fullerenes [24] were also found to be carbon sources for the synthesis of MWCNTs.

In 2010, Plata et al. [29] added small amounts of hydrocarbons, ethylene, and hydrogen to the reactor. The results show that the addition of alkanes can promote the synthesis of MWCNTs. Therefore, they demonstrate a unique mechanism for the formation of carbon nanotubes, which is quite different from the previously known; they believe that the carbon source may not decompose during C—C bond formation.

SWCNTs can be synthesized from toluene, methane, benzene, phenylacetylene, fullerene, and cyclohexane [6] as carbon sources.

By selecting a suitable carbon source and its gas pressure, the yield, quality, and purity of the carbon nanotubes can be simultaneously improved.

In 2002, Maruyama et al. [30] presented a report on the synthesis of high-purity SWCNTs from ethanol on a double-impregnated zeolite matrix at low temperatures. The advantage of ethanol as a carbon source is that the CNTs produced have almost no amorphous carbon. Since that, ethanol has become a commonly used carbon source for CVD synthesis of CNTs. The low price of ethanol can greatly reduce the cost, making the production of carbon nanotubes almost free. Subsequently, vertically aligned SWCNTs were also found to grow on silica and silicon substrates under the action of molybdenum and cobalt bimetallic catalysts [31, 32]. Recently, Maruyama's research team found that intermittent supply of acetylene can significantly help ethanol to maintain catalyst activity, thereby increasing the growth rate of carbon nanotubes [33].

In 2004, Hata et al. [34] reported that impurity-free SWCNTs could be efficiently synthesized on Si substrates using water assisted ethylene CVD. They proposed that the amorphous carbon can be selectively removed without damaging the CNTs in growth by controlling the water vapor supply to the CVD reactor as a weak oxidant. Balancing the relative content of ethylene and water is very important for prolonging the service life of the catalyst. Joshi et al. [35] produced ultra-long CNTs in 2010 using ethylene as a carbon source, assisted by hydrogen and water vapor. This study found that in order to generate super-long and high-quality CNTs on catalysts composed of complex surfaces, the hydrogen/water ratio should be very accurate.

In addition to the above conventional carbon sources, some organic compounds can also be used as carbon sources for the growth of carbon nanotubes, especially polymers, carbonization of poly-acrylonitrile, poly-furfuryl-alcohol, amino-dichloro-s-triazine [6], and carbonization of polymers.

Tripropylamine was pyrolyzed in the AFI nanochannel (0.73 nm) to obtain the nanotubes with the smallest diameter (0.4 nm) [36]. In 2009, Han [37] obtained the required MWCNT diameter by loading some polymer carbon source in a well-defined pore size on the alumina template carbonization with a temperature range of 400–600°C.

In recent years, metallic organic compounds, such as metallocene complex (cobalt diene, ferrocene, and nickelocene) [38] and nickel phthalocyanine [39],

have been used as carbon sources and catalysts at the same time. Although CNTs grown have high metal encapsulation, their yields are very low.

Zdrejek et al. [40] demonstrated that CVD can be used to synthesize high quality SWCNTs and MWCNTs at a range of temperatures using pure propane as a carbon source in 2015. In their research report, it is proposed that adjusting the growth temperature can control the volume of carbon nanotubes. Cui et al. [41] synthesized a thin-walled, open-type N-doped CNT array by floating CVD, in which the carbon source was acetonitrile. The product obtained has a large thin-wall index, which is defined as the ratio of the inner diameter of the CNTs to the wall thickness.

In addition, CNTs can be successfully synthesized from kerosene, liquefied petroleum gas, gas, natural gas, waste plastics, green grass [6], and other daily raw materials as carbon sources. In addition, Terrones et al. [42] loaded a cobalt catalyst on a silica substrate by laser etching and then produced an oriented carbon nanotube by pyrolyzing 2-amino-4,6-dichloro-pyrolis. This study demonstrates that the use of patterned catalysts significantly promotes the formation of aligned nanotubes.

Kumar et al. [43] used camphor to grow carbon nanotubes on a nanoporous zeolite substrate and first proposed optimized conditions for growing SWCNTs and MWCNTs. Brazilian scientists [21] conducted thermal annealing and

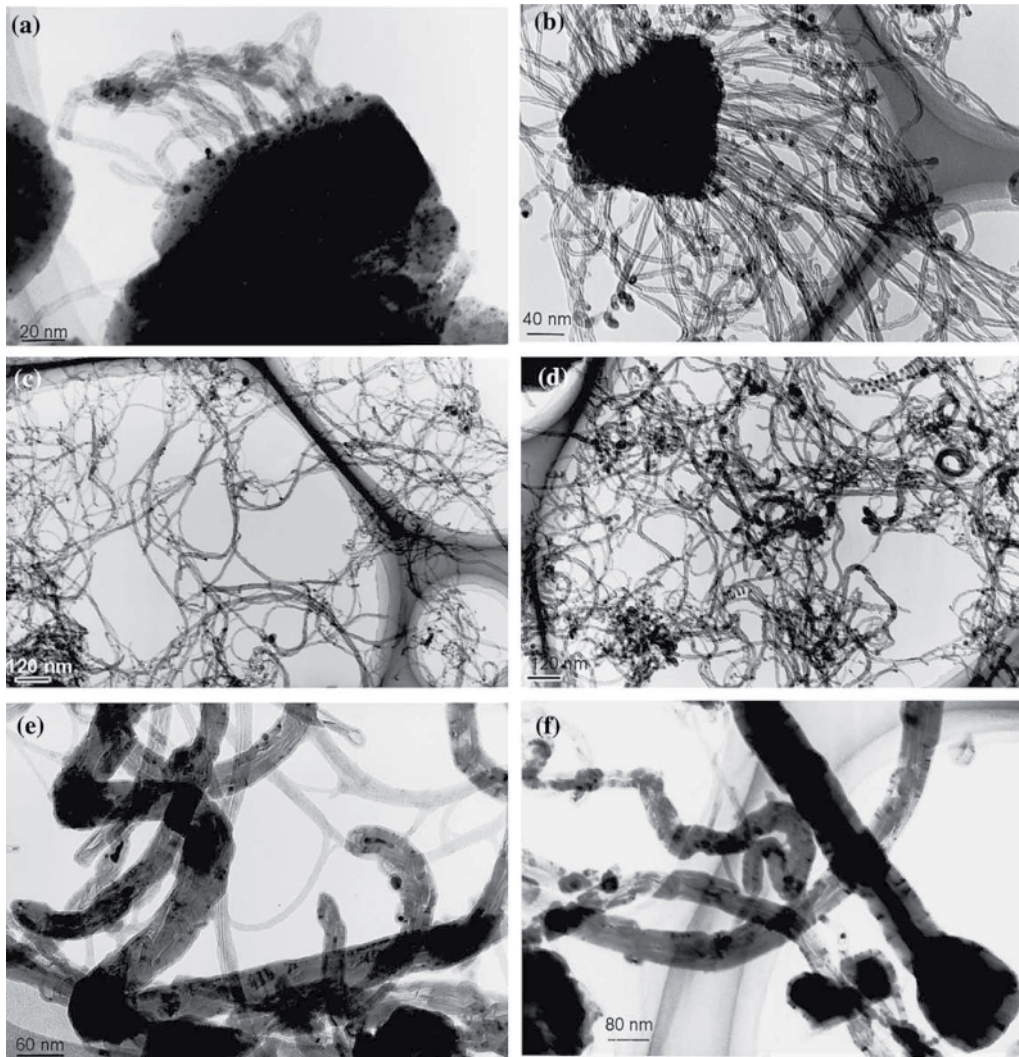


Figure 4. Carbon nanotubes produced by camphor at different temperatures. Reproduced with permission of Ref. [43].

electrochemical purification of CNTs grown in camphor, and in China, Tang et al. [44] used ferrocene as a catalyst and camphor as a carbon source, in the argon atmosphere, prepared multi-branched dendritic carbon by CVD, and announced the effects of reaction temperature, carrier gas flow rate, and ferrocene density on the structure of CNTs. Subsequently, they published hydrogen storage analyses for different types of CNTs [45]. Therefore, camphor is a promising and efficient new carbon source. There is no doubt that this is an energy-saving way. As an agricultural product, camphor is definitely a renewable raw material; therefore, there is no danger of depletion of natural resources. Therefore, the synthesis of carbon nanotubes based on camphor largely conforms to the principles of green chemistry. This work caught the attention of industrial ecologists (**Figure 4**).

Subsequently, cheap raw materials such as turpentine [46–48] and eucalyptus oil [49] have also been reported for growth of CNTs.

In nanoelectronics, SWCNTs are more popular than MWCNTs because of their properties and bandgap displacement due to small changes in the diameter and wrapping angle of the nanotubes, but this property of SWCNTs can only be fully exploited if they are structurally pure.

Therefore, in the past 20 years, the biggest challenge facing the scientific community is how to control the generation process of CNTs and obtain SWCNTs with a single structure. Researchers are currently working on how to control their chirality when generating SWCNTs.

In 2013, He et al. [50] reported the use of carbon monoxide as a carbon source, giving priority to under 500°C to generate very high density of CNTs. Yang et al. [51] stated that chiral SWCNTs were directly synthesized from solid alloy catalysts with ethanol. Both experiments and simulations have shown that the highly selective growth of SWCNTs is that the catalyst has a high melting point, so that they can maintain the crystal structure during chemical vapor deposition.

In fact, under certain experimental conditions, any containing carbon can be used as a carbon source. It is necessary to identify cheap carbon sources that can control chiral growth of CNTs under CVD in the future.

4. Catalyst

The catalyst is indispensable in the process of preparing CNTs by the CVD method. It can reduce the decomposition temperature of the carbon source and promote the nucleation of CNTs, which is the most important influencing factor for the preparation of CNTs. Specific carbon nanotube synthesis requires different catalysts. Synthetic SWCNTs usually require nanosized particles as catalysts, and MWCNTs can also be produced without catalysts. At present, the preparation process of multi-walled CNTs is quite mature, and industrial production has been realized by the CVD method. The production cost of single-walled CNTs is still quite high, and the preparation of macroscopic array single-walled CNTs has not been realized.

Catalyst is the carbon source decomposition active center and graphite carbon deposition center in the growth process of CNTs. The selection, preparation, and carrier selection of CNTs will also be very important for nucleation, growth rate, density, separation, and purification of CNTs. This large influence can lead to the different morphology and structure of CNTs, which is significant for the preparation of CNTs. The results showed [52, 53] that the effective dispersion of catalyst particles is one of the key factors in the synthesis of CNTs, and the size of catalyst particles directly determines the diameter of CNTs.

Therefore, the preparation of a catalyst having a specific particle diameter with high catalytic activity, high selectivity, and good dispersibility is the key to whether the CVD method can mass produce high-purity CNTs. The catalysts prepared by different methods have different dispersibilities and large difference in catalytic activity, which results in different carbon nanotube content and tube diameter. The composite catalyst prepared by the same method has a closely related relationship between the catalytic activity and the ratio of the effective component and the carrier, and the optimum ratio.

Some popular transition metal nanoparticles are usually used as catalysts in CVD synthesis of CNTs [54]. It is reported that Fe, Co, Ni, Pd, Pt, Au, Mn, W, Ti, Co, Mg, Al, In, Na, K, Cs, and other metals reported can be used in the preparation of MWCNT in recent years, and the diameter of these catalyst nanoparticles is usually larger than 3 nm. Single-walled CNTs are usually produced when the active components of Fe, Co, Ni, Pd, Pt, Ru, Cu, Ag, Au, Mn, Cr, Mo, and other metals act as catalysts, and the particle size of the generated nanoparticles is often less than 3 nm.

Due to the high carbon solubility of Fe, Co, and Ni, transition metal carbides can be formed. With a high diffusion rate in these transition metals, nucleation and growth of carbon atoms can be carried out [55]. Cu, Au, Ag, Pt, and Pd can also be used to synthesize CNTs by catalyzing appropriate carbon sources [56]. Among the catalysts, transition metals (Fe, Co, and Ni) are the most widely studied and widely used catalyst for the nucleation and growth of CNTs due to their relatively high carbon solubility and carbon diffusion coefficient. They are more effective in forming SWCNTs [21]. In addition, due to the high melting point of these metals and the low equilibrium vapor pressure, this provides a wide range of CVD temperatures for various carbon sources and can be used to grow carbon nanotubes at different temperatures. It is worth noting that transition metals are not only effective catalysts in CVD, but are also effective catalysts in other preparation processes.

Solid organometallic metallocene compound (ferrocene, cobalt, nickel-ene) is widely used as carbon nanotube catalysts for the reason that they can release metal nanoparticles, resulting in more effectively catalyzing the decomposition of hydrocarbons. Chaisitsak et al. [57] have also prepared single-walled CNTs by floating catalytic method by using ferrocene as a catalyst and ethanol as a carbon source. Other nanoparticles can also be used as catalysts for the synthesis of CNTs, such as diamond and semiconductor nanoparticles (Si and Ge). Chemical vapor deposition is employed to grow single-walled CNTs on sapphire substrates [58]. In addition, CNTs were grown on scratched silicon wafers [59] without any other catalyst. The growth of CNTs does not require metal at all, and the nonmetallic matrix itself can be used as a catalyst. The synthesis of metal-free CNTs (MWCNTs) is undoubtedly a breakthrough in the research of CNTs and opens up a new approach to nanotechnology.

SWCNTs have many excellent properties, and their atomic scale changes resulted diversity. They are still limited by large-scale, high-purity, ordered, and specific chiral controllable preparations. Single-walled CNTs undergo nucleation growth and structural regulation on the catalyst.

In 1996, Dai et al. [60] realized the synthesis of single-walled CNTs in the chemical vapor deposition (CVD) using Mo or Ni-Co catalysts. Bachilo et al. [61] obtained single-walled CNTs using Co-Mo alloy catalyst in 2003. In 2004, Hata et al. [34] prepared single-walled carbon nanotube vertical arrays using Fe as a catalyst. In conclusion, the catalysts for the synthesis of single-walled CNTs are generally Fe, Co, Ni, or bi-metallic compound catalysts.

Shin et al. [62] used Ni-based and Fe-based catalytic systems, and high-yield synthesis of SWCNTs was demonstrated. It is more difficult to synthesize SWNTs with a low temperature in nickel-based catalyst system than in iron-based catalyst system. It is likely related to the diffusion rate and carbon solubility of the catalyst

metal. Jafarpour et al. [63] found that the double-layer catalyst for preparing Co–Mo: 0.5–0.1 nm at low deposition rate has a high prospect of application, because in this special structure, not only high quality but also long vertical SWNTs can be obtained. SWCNT thin films with high semiconductor content can also be obtained. Mendoza et al. [64] declared the influence of molybdenum for CVD synthesis of MWCNTs. The addition of a molybdenum-based catalyst based on magnesium oxide to a cobalt catalyst has a significant effect on the production of carbon nanotubes.

In 2002, Harutyunyan et al. [65] used methane to grow CNTs on alumina substrates using two catalysts, respectively, Fe and Fe/Mo two-component catalysts. It revealed that molybdenum had obvious synergistic effect, decreased the growth temperature, and it also eliminated the process of catalyst activation in hydrogen. Molybdenum is widely used as a cocatalyst in metal supported catalysts because it can increase the yield of CNTs. In addition, molybdenum is a significant promoter added to the iron-based catalyst, which increases the activity of the catalyst at lower temperatures.

In early reports, bi-metallic and tri-metallic compound catalysts can solve many problems of CNT productions. Iron plays a higher catalytic role in the decomposition of hydrocarbons, which leads to the increase of CNT deposition, but the graphitization degree of these CNTs descends. On the other hand, cobalt catalyst makes carbon nanotube graphitization superior, but the yield decreases. Therefore, the attempt to mix the advantages of two metals is successful, and the multicomponent catalyst is considered to be a better catalyst than the pure metal.

In addition to the composition of the catalyst, the preparation conditions of the different catalysts also have an effect on the growth of the CNTs. Flahaut et al. [66] used urea or citric acid as raw material to prepare catalysts by combustion. Studies have found that milder combustion conditions can limit the formation of carbon nanofibers, thereby increasing the selectivity to SWCNTs. Chang et al. [67] took Fe and Ni as an example, and they found that the composition and size of the bicomponent metal catalyst is the key to the large-scale preparation of single-walled CNTs.

In addition to the catalyst materials, the concentration of catalyst is also vital in the growth of CNTs. Lower concentration of catalyst (2.4–5%) showed that SWCNT increased (1–50% and above), while high concentration of Fe and Co was beneficial to the growth of MWCNTs. The yield of MWCNTs prepared with 40% Fe and Co catalyst concentration is the highest and the metal pollution is negligible [68]. These studies confirmed that the proper selection of catalyst materials and their concentrations can selectively culture SWCNTs or MWCNTs.

In the experiment of Zarabadi-Poor et al. [69], they first loaded the metal component iron on alumina, and then decomposed methane at 1000°C to prepare CNTs. Studies have shown that the diameter and length of the CNTs depend on two experimental conditions, one for the iron content of the catalyst and one for the reaction time. Thinner CNTs can be obtained at lower iron concentrations. In addition to affecting the diameter and length of CNTs, the concentration of iron also affects morphological control. As the concentration of iron in the catalyst increases, carbon tends to form carbon nanoribbons rather than carbon nanotube structures.

The proper calcination temperature can regulate the interaction between the active center and the support, make the active metal easy to reduce, and reduce the particle diameter of the catalyst, and ultimately affect the activity of the catalyst and the morphology and properties of the carbon product.

The general rule of thumb is that MWCNTs are easier to form at 600–900°C, and more favorable for SWCNT growth at 900–1200°C. Temperature has a great influence on the growth of CNTs: the higher the growth temperature, the better the degree of graphitization of CNTs, and the higher the yield of CNTs than at low temperature [70]. But it is easy to form carbon structure with five-member ring at too high temperature, which leads to defective CNTs with different shapes [71].

In addition to particle size and morphology, the influence of atmosphere on the catalyst may also change the properties of CNT by influencing the structure of the catalyst. Harutyunyan et al. [72] designed cleverly Ar/He/H₂/H₂O pretreatment gas effectively to increase the proportion of metallic SWCNTs. In 2014, Bayer et al. [73] used Co/SiO₂ to catalyze the growth of SWCNTs with concentrated chiral and pipe diameter distribution. The only explanation for the variation was the effect of ammonia pretreatment on the catalyst's valence state and particle size distribution.

In the process of CVD synthesis of CNTs, water vapor, oxygen (air), and ethanol are added into the growth atmosphere, and they can selectively remove amorphous carbon without damaging the nanotube and significantly improve the activity and life of the catalyst.

Hata [34] succeeded in production of SWNTs using a variety of catalysts including Fe nanoparticles from FeCl₃, silicon wafers, quartz, and metal foil sputtering metal films (Fe, Al/Fe, Al₂O₃/Co). The catalytic activity induced by water stimulation resulted in dense and vertically arranged SWNT forest.

Li et al. [74] prepared extremely long and compact CNT beams on ferrocene by air-assisted chemical vapor deposition in 2008. Air-assisted CVD can prolong the service life of the catalyst and rapidly synthesize long and well-arranged carbon nanotube bundles up to 1.5 cm in length.

Water-assisted chemical vapor deposition was used to synthesize hyper-beam single-walled CNTs by Zhao et al. [75] in 2015. Water vapor was introduced into the reactor and the yield of SWCNT was significantly increased from 40 to 206 wt.%. By adding water vapor, the average diameter of SWCNTs increases from 1.5 to 3.0 nm and the diameter distribution becomes broader.

In addition to the carrier gas and the reducing gas in the CVD process, it is also possible to add water vapor or ethanol in an auxiliary manner, which not only increases the yield of the carbon nanotubes, but also increases the activity of the catalyst.

5. CNT substrates

During the growth of CNTs, the catalyst needs to be supported on a suitable matrix to ensure the quality and yield of the CNTs, including the material, surface topography, and texture properties of the matrix. The various substrates used for CNT growth in CVD are silicon, silicon carbide, graphite, quartz, silica, alumina, magnesium oxide, calcium carbonate, zeolite, sodium chloride [6], and so on. The most commonly used catalyst substrates are silica, zeolite, and alumina. Among these catalyst-based materials, magnesium oxide is the most operative substance for producing SWCNTs.

Mattevi et al. stated [76] that alumina is a better catalyst carrier than silicon dioxide because of its strong metal-carrier interaction, high metal dispersion, and high catalytic site density. They used X-ray photoelectron spectroscopy to study the interaction of the catalyst with the catalyst support during the CVD process over a wide range of pressures. Due to the particularity of Fe/Al₂O₃ interface reaction, the addition of the Al₂O₃ support layer can increase the yield of CNTs. They observed that the carrier interaction of Al₂O₃ is much solidier than that of SiO₂, which limits the surface fluidity of the iron.

In 2007, Noda et al. [77] found that there were significant differences between Al₂O_x and Al₂O₃ for the catalysts. When the particle size distribution of iron was relatively more than 0.6 nm, nanotube forests grew thicker in either catalyst. When the particle size distribution of iron was less than 0.6 nm, nanotube forests can only grow thicker under the catalyst of Fe/Al₂O_x catalyst. Al₂O_x catalyst carrier was more suitable than Al₂O₃ for the growth of SWCNTs.

Grain boundaries or grain grades of supporting materials play an irreplaceable role for synthesis of CNTs. Mattevi et al. [76] showed that the high-valence state of iron does not decrease during CNT synthesis, presumably related to the details of the interface between iron and alumina. The generation of a large amount of lattice strain in the metal particles is the root cause of this dynamic stability.

Some porous materials such as Al_2O_3 , MgO , and zeolites are used as catalyst supports in order to obtain smaller and uniformly dispersed catalyst particles. In particular, some catalytic studies based on silica gel or zeolites support show that porous materials are excellent carriers for the production of CNTs. By making metal particles distribute uniformly in the support, the problems of agglomeration and enrichment of metal catalyst particles can be solved very well. Lee et al. [78] using porous SiO_2 as carrier first obtained a three-dimensional network of single-walled CNTs by chemical vapor deposition at 800°C .

However, a large amount of amorphous carbon tends to accumulate in the pores of porous materials, and the preparation of CNTs requires an extra step of purification, which may cause additional pollution or structural damage of CNTs. Couteau et al. [79] could overcome these difficulties by using CaCO_3 as a catalyst carrier. CaCO_3 is not a porous material, which decreases the production of amorphous carbon. Moreover, both metal particles and catalyst carriers can be dissolved in dilute inorganic acids, so CNTs with high yield and high purity can be obtained.

The catalyst substrate not only functions as a carrier, but also interactions between the substrate and the catalyst, chemical interactions, and physical interactions may occur, such as van der Waals forces and static forces. The physical interaction prevents the movement of the catalyst particles on the support material, and also reduces the thermal diffusion and sintering of the metal particles on the matrix material, which makes the particle size distribution of the catalyst tend to be stable during the synthesis of the carbon nanotubes. The chemical interaction also helps to maintain the particle size distribution of the catalyst particles.

Studies have found that some precious metals can also be used as catalyst active ingredients for growing CNTs. CNTs doped with heteroatoms (such as nitrogen) can enhance the bonding of metals to CNTs. Lv et al. [80] first synthesized high purity, open and well-aligned N-CNTs-graphenes by water-assisted CVD and then used them as support materials for noble metal nanoparticles. The results demonstrated that the electronic structure (N-doped) and the hierarchical structure (graphite-CNT hybridization) are improved.

6. Conclusion and future perspectives

To sum up, the formation of metal catalyst nanoparticles is extremely important for CVD synthesis of CNTs. Nanoparticles must be formed on the surface of a nonconductive substrate, which is conducive to the formation of these nanoparticles. The yield and quality of CNTs are greatly affected by the matrix material. The surface morphology and grain size of the matrix can greatly affect the quality and alignment of the carbon nanotubes. In addition, the substrate thickness of the catalyst has significant impact on the growth rate of the CNTs.

Chemical vapor deposition is an ideal and effective method for the preparation of large-scale chiral CNTs with low cost, high carbon source rate, high product purity, and easy control. Chiral growth control is the ultimate goal of CNTs. Its realization marks the controllable synthesis of CNTs in diameter, wall number, helicity, chiral angle, and structure. It can greatly promote the wide application of CNTs in micro-nanoelectronic devices, sensors, intelligent functional materials, optical devices, and other fields.

Catalyst type, catalyst particle size, carbon source gas type, and reaction temperature are the main factors affecting the yield and performance of CNTs. Finding suitable catalyst type and particle size, suitable carbon source gas, and reaction temperature is the prerequisite for large-scale preparation of high-quality CNTs. In the process of CNTs synthesis by the CVD method, there is still a lot of room for exploration.

1. The reason of catalytic activity of transition metal catalyst needs to be further analyzed.
2. To find a way to control the particle size of the catalyst and provide a possible method for preparing CNTs with specific layers and morphologies.
3. Chiral control is more challenging. The controlled preparation of single-walled CNTs with uniform structure, macroscopic length, single chirality, and excellent properties has always been a research focus.
4. How to selectively produce CNTs with specific morphology and properties?
5. How to improve the growth rate of CNTs, what is the most important step? What are the crucial steps in nucleation progress?
6. The growth of CNTs is currently highly dependent on high temperature environments. Finding a way to grow CNTs at room temperature is a big challenge.
7. When large quantities of CNTs are produced, they often contain many magazines, whether they are catalyst particles, substrates, or amorphous carbon, which require further processing. However, purification will greatly reduce the quality and final yield of CNTs, and more thinking is needed to achieve high purity growth.

Author details


Xiao-Di Wang¹, K. Vinodgopal² and Gui-Ping Dai^{1*}

1 School of Resources, Environmental and Chemical Engineering,
Nanchang University, Nanchang, Jiangxi, China

2 Department of Chemistry and Biochemistry, North Carolina Central University,
Durham, NC, USA

*Address all correspondence to: nanodai@gmail.com

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