Growing carbon nanotubes

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The discovery of ‘fullerenes’ added a new dimension to the knowledge of carbon science; and the subsequent discovery of ‘carbon nanotubes’ (CNTs, the elongated fullerene) added a new dimension to the knowledge of technology. Today, ‘nanotechnology’ is a hot topic attracting scientists, industrialists, journalists, governments, and even the general public. Nanotechnology is the creation of functional materials, devices, and systems through control of matter on the nanometer scale and the exploitation of novel phenomena and properties of matter (physical, chemical, biological, electrical, etc.) at that length scale. CNTs are supposed to be a key component of nanotechnology. Almost every week a new potential application of CNTs is identified, stimulating scientists to peep into this tiny tube with ever increasing curiosity.

CNTs, born in the Ando lab and introduced to the world by Iijima, are now 13 years old and much has been said, written, and discussed about this teenage hero of the scientific Hollywood. The immediate challenge is to produce CNTs of desired properties in large quantities. The essence of this challenge lies in understanding the growth mechanism of CNTs, which is not yet clear. In this review, therefore, we focus on the synthesis aspect only, pointing out the products, problems, and limitations of the available CNT growth techniques. Although there have been many interesting and successful attempts to grow CNTs by various methods, we restrict our discussion to the three most widely used techniques: arc discharge, laser furnace, and chemical vapor deposition (CVD).

Arc-discharge method

The arc-discharge method is the one by which CNTs were first produced and recognized. The history of CNTs is closely related to the mass production of fullerenes developed by Kratschmer et al. in 1990. They evaporated graphite rods in contact by applying an ac voltage in an inert gas to produce fullerenes. Soon after, we applied a dc arc voltage between two separated graphite rods (Fig. 1) by modifying our SiC powder production apparatus. The evaporated anode generates fullerenes in the form of soot in the chamber, and a part of the evaporated anode is deposited on the cathode. In that cathode deposit, Iijima found the treasure, CNTs.

The schematic diagram of CNT production apparatus is shown in Fig. 1. After evacuating the chamber with a vacuum...
pump, an appropriate ambient gas is introduced at the desired pressure, and then a dc arc voltage is applied between the two graphite rods. When pure graphite rods are used, the anode evaporates to form fullerenes, which are deposited in the form of soot in the chamber. However, a small part of the evaporated anode is deposited on the cathode, which includes CNTs. These CNTs, made of coaxial graphene sheets and called multi-walled carbon nanotubes (MWNTs), are found not only on the top surface of the cathode deposit but also deep inside the deposit. Large-scale synthesis of MWNTs by arc discharge has been achieved in He gas, and their thermal purification has also been successful. When a graphite rod containing metal catalyst (Fe, Co, etc.) is used as the anode with a pure graphite cathode, single-walled carbon nanotubes (SWNTs) are generated in the form of soot. The first author of this review, Ando, has been carrying out the arc-discharge evaporation of pure graphite rods in various kinds of ambient gases (He, Ar, and CH₄) since CNTs were first discovered. It was found that CH₄ gas was the best for forming MWNTs with high crystallinity and few coexisting carbon nanoparticles. On the contrary, fullerenes cannot be produced in gas including hydrogen atoms. This is the essential difference between CNT and fullerene production. In order to clarify the effect of gas including hydrogen atoms in MWNT production, ambient CH₄ gas was analyzed before and after arc discharge by mass spectroscopy, which revealed that the thermal decomposition of CH₄ gas is as follows: 2CH₄ → C₂H₂ + 3H₂. Therefore, pure graphite rods were arc evaporated in pure hydrogen gas. The effectiveness of hydrogen arc discharge in producing MWNTs with high crystallinity was confirmed, and a new morphology of carbon, the ‘carbon rose’, was also found. A similar effect of ambient hydrogen gas was also reported by another group. In fact, for MWNT production, a gas that includes hydrogen atoms is more effective than an inert gas, such as He or Ar. The reason might be the high temperature and high activity of the hydrogen arc.

The MWNTs produced by hydrogen arc discharge (H₂-arc MWNTs) contain very few coexisting carbon nanoparticles, as seen in the scanning electron micrograph of Fig. 2a. These nanoparticles are easily removed by infrared irradiation or heating in air at 500°C. For instance, thermally purified MWNTs are shown in Fig. 2b. High-resolution transmission electron microscopy observation of the purified H₂-arc MWNTs reveals that their crystallinity is very high (having regular graphene sheets at an interlayer spacing of 3.4 Å) and an inner diameter typically as low as 7 Å, which is equal to the diameter of C₆₀. Until the beginning of this year, the smallest nanotube known was 4 Å in diameter (Fig. 3a). However, very recently 3 Å tubes have been found to exist inside H₂-arc MWNTs (Fig. 3b). Moreover, a linear carbon chain has also been observed inserted into an MWNT with an innermost tube diameter of 7 Å. Surprisingly, both the 3 Å tube and the carbon chain exist in the same H₂-arc MWNTs.
Corresponding to these thin innermost tubes in H$_2$-arc MWNTs, radial breathing modes (RBM) in Raman spectra are observed$^{24,25}$. It is well known$^{26}$ that the wave number, $\omega$, of RBM is inversely proportional to the tube diameter, $d$. From the Raman spectra, it is clear that H$_2$-arc MWNTs have an innermost tube diameter that is smaller than independently produced SWNTs. In the high wave number region ($\sim$1580 cm$^{-1}$) of the Raman spectra, isolated H$_2$-arc MWNTs exhibit splitting of the G-band$^{27}$, which is usually only found in SWNTs. This is characteristic of the quantum confinement effect$^{27}$ because of the very thin diameter of CNTs.

The experimental history of SWNTs$^{12,13}$ starts two years after the discovery of MWNTs$^2$. SWNTs were also first produced by arc discharge using a graphite anode containing a metal catalyst (Fe or Co); however, SWNTs were obtained from the soot in the gas phase not from the cathode deposit. Of course, evaporated metal nanoparticles also coexist with the SWNTs, which have to be purified later.

Mass production of SWNTs by arc discharge was achieved by Journet et al.$^{28}$ using a bimetallic Ni-Y catalyst in He ambient gas. The method was effectively modified$^{29}$ by using two graphite electrodes inclined at an angle of 30° instead of the conventional 180° alignment. This is known as the arc-plasma-jet method$^{29}$ and yields SWNTs at a rate of \( \sim 1 \) g/min. Another method$^{30}$, using an Fe catalyst instead of Ni-Y and an H$_2$-Ar gas mixture in place of He, produces a partly aligned macroscopic net of SWNTs as long as 30 cm (Fig. 4). Because the Fe nanoparticles attached to the SWNT net are covered with a very thin layer of amorphous carbon, the SWNTs are easily purified by heating in air at 420°C and then rinsing in mild HCl.
In order to produce SWNTs, the use of metal catalysts is a necessary condition. The activities of various kinds of metal catalysts (Ni, Co, Fe, Pt, Pd, etc.) have been investigated and the maximum yield is achieved with Ni-Co. It was also observed that the addition of S increases the catalytic effect of other metal catalysts. Double-walled nanotubes produced by arc discharge have also been reported under conditions similar to those of large-diameter SWNT formation. It may be noted that SWNTs are not found in the cathode deposit like MWNTs but in the chamber soot. Therefore, an ac arc discharge, in which both the electrodes evaporate alternately, can produce a higher yield of SWNTs.

Generally, it is hard to grow aligned CNTs (SWNTs, DWNTs, or MWNTs) by arc discharge, although partial alignment of SWNTs can be achieved by convection or directed arc plasma. On the other hand, the growth temperature of the arc-discharge method is higher than that of other CNT production methods. As a result, the crystallinity and perfection of arc-produced CNTs are generally high, and the yield per unit time is also higher than other methods.

**Laser-furnace method**

The laser vaporization method, which had been originally used as a source of clusters and ultrafine particles, was developed for fullerene and CNT production by Smalley’s group. Since the energy density of lasers is much higher than that of other vaporization devices, the laser is suitable for materials with a high boiling temperature such as carbon. When applied to carbon, fullerenes were discovered by mass spectrometry but their structural identification was impossible at that time because their quantities were too small. To produce large quantities of fullerenes and other nanomaterials, Smalley’s group developed the laser-furnace method together with an annealing system in 1992. Fullerenes with a soccer ball structure are produced only at higher furnace temperatures, underlining the importance of annealing for nanostructures. These discoveries were applied to produce CNTs in 1996, especially SWNTs.

Fig. 5 shows the setup of the laser furnace, which consists of a furnace, a quartz tube with a window, a target carbon composite doped with catalytic metals, a water-cooled trap, and flow systems for the buffer gas to maintain constant pressures and flow rates. A laser beam (typically a YAG or CO₂ laser) is introduced through the window and focused onto the target located in the center of the furnace. The target is vaporized in high-temperature Ar buffer gas and forms SWNTs. The Ar flow rate and pressure are typically 1 cm·s⁻¹ and 500 torr, respectively. The SWNTs produced are conveyed by the buffer gas to the trap, where they are collected. The vaporization surface is kept as fresh as possible by changing the focus point or moving the target.

The method has several advantages, such as high-quality SWNT production, diameter control, investigation of growth dynamics, and the production of new materials. High-quality SWNTs with minimal defects and contaminants, such as amorphous carbon and catalytic metals, have been produced using the laser-furnace method together with purification processes. High crystallinity has been known to originate in high-power laser vaporization, homogeneous annealing conditions, and target materials without hydrogen. The laser has sufficiently high energy density not to cleave the target into graphite particles but to vaporize it at the molecular level. The graphite vapor is converted into amorphous carbon as the starting material of SWNTs. The annealing conditions of the amorphous carbon are more homogeneous than those of the arc-discharge method, in which the electrodes and the convection flow disturb the homogeneity of the temperature and flow rate.

To achieve homogeneous conditions in arc discharge, a method called high-temperature pulsed arc discharge has been developed, which uses a dc pulsed arc discharge inside a furnace. The method provides high-quality DWNTs and SWNTs. It can be considered a hybrid of steady arc discharge and the laser-furnace method. The SWNTs still have contaminants, such as amorphous carbon and catalytic metals. To remove these contaminants, purification processes...
based on oxidation by hot air (400-500°C) or chemicals such as H₂O₂ are applied to the crude SWNTs. Amorphous carbon has many dangling bonds, which are not present in SWNTs, leading to high activity. High-quality SWNTs with few defects are more resistant to oxidation treatments than those of low quality. The oxidation treatments remove the protective layer of catalytic metal particles so that they are easily eliminated by acid treatments.

SWNT diameter can be controlled by changing the furnace temperature, catalytic metals, and flow rate. A higher furnace temperature results in SWNTs with larger diameters. The use of a Ni-Y alloy catalyst also increases the SWNT diameter, whereas a Rh-Pd catalyst reduces it. Flow rate affects the diameter distribution, which suggests that the growth process is fairly slow (on a timescale of seconds) compared with vaporization processes. SWNT growth is initiated by a short laser shot, so that the start time of the growth is defined. The growth processes have been traced by high-speed video imaging of light emission or scattering, from which the growth time is estimated to be more than several milliseconds.

Novel nanomaterials, such as peapods and single-walled carbon nanohorns (SWNHs), are also produced by the laser-furnace method. Peapods, fullerenes encapsulated by SWNTs, were discovered in the soot of the laser furnace and later synthesized from isolated fullerenes and laser-produced, purified SWNTs. The fullerenes are sublimated and introduced into SWNTs through open ends or holes in the wall at a high vacuum (~10⁻⁶ torr) at 500-600°C. Since these vacancies are easily covered with amorphous carbon because of their active edges, purified SWNTs grown by the laser-furnace method are indispensable for maximizing the peapod yield. SWNHs, small hollow carbon edging particles, have been discovered in the carbon soot when using a CO₂ laser. SWNHs have a large surface/volume ratio and are promising as a support material for fuel cell catalysts. In SWNH production, a CO₂ laser with a long pulse duration (a few milliseconds) is crucial; SWNHs cannot be produced with a short-pulsed YAG laser (pulse durations of nanoseconds). A longer pulse duration, which leads to a lower energy density and lower vaporization temperature, is essential for the production process. The tunable duration of laser vaporization is another advantage in producing and exploring these nanoscale carbon materials. That is why the laser-furnace method is being used for growing various nanomaterials, and is expected to play a powerful role in nanotechnology.

**Chemical vapor deposition**

CVD is another popular method for producing CNTs in which a hydrocarbon vapor is thermally decomposed in the presence of a metal catalyst. The method is also known as thermal or catalytic CVD to distinguish it from the many other kinds of CVD used for various purposes. Compared with arc-discharge and laser methods, CVD is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure, at the cost of crystallinity. It is versatile in that it harnesses a variety of hydrocarbons in any state (solid, liquid, or gas), enables the use of various substrates, and allows CNT growth in a variety of forms, such as powder, thin or thick films, aligned or entangled, straight or coiled, or even a desired architecture of nanotubes at predefined sites on a patterned substrate. It also offers better control over growth parameters.

In fact, CVD has been used for producing carbon filaments and fibers since 1959. Endo et al. reported CNT growth from pyrolysis of benzene at 1100°C, while José-Yacamán et al. formed clear helical MWNTs at 700°C from acetylene. In both cases, Fe nanoparticles were used as the catalyst. Later, MWNTs were also grown from ethylene, methane, and many other hydrocarbons. SWNTs were first produced by Dai et al. from disproportionation of CO at 1200°C, catalyzed by Mo particles. Later, SWNTs were also produced from benzene, acetylene, ethylene, and methane using various catalysts.

Fig. 6a shows a diagram of the setup used for CNT growth by CVD in its simplest form. The process involves passing a hydrocarbon vapor (typically for 15-60 minutes) through a tube furnace in which a catalyst material is present at sufficiently high temperature (600-1200°C) to decompose the hydrocarbon. CNTs grow over the catalyst and are collected upon cooling the system to room temperature. In the case of a liquid hydrocarbon (benzene, alcohol, etc.), the liquid is heated in a flask and an inert gas purged through it to carry the vapor into the reaction furnace. The vaporization of a solid hydrocarbon (camphor, naphthalene, etc.) can be conveniently achieved in another furnace at low temperature before the main, high-temperature reaction furnace shown in Fig. 6a. The catalyst material may also be solid, liquid, or gas.
and can be placed inside the furnace or fed in from outside. Pyrolysis of the catalyst vapor at a suitable temperature liberates metal nanoparticles in situ (the process is known as the floating catalyst method). Alternatively, catalyst-plated substrates can be placed in the hot zone of the furnace to catalyze CNT growth. Catalytically decomposed carbon species of the hydrocarbon are assumed to dissolve in the metal nanoparticles and, after reaching supersaturation, precipitate out in the form of a fullerene dome extending into a carbon cylinder (like the inverted test tube shown in Fig. 6b) with no dangling bonds and, hence, minimum energy²⁷,²⁸. When the substrate-catalyst interaction is strong, a CNT grows up with the catalyst particle rooted at its base (known as the ‘base growth model’). When the substrate-catalyst interaction is weak, the catalyst particle is lifted up by the growing CNT and continues to promote CNT growth at its tip (the ‘tip growth model’). Formation of SWNTs or MWNTs is governed by the size of the catalyst particle. Broadly speaking, when the particle size is a few nanometers, SWNTs form, whereas particles a few tens of nanometers wide favor MWNT formation.

The three main parameters for CNT growth in CVD are the hydrocarbon, catalyst, and growth temperature. General experience is that low-temperature CVD (600–900°C) yields MWNTs, whereas a higher temperature (900–1200°C) reaction favors SWNT growth, indicating that SWNTs have a higher energy of formation (presumably owing to their small diameters, which results in high curvature and high strain energy). This could explain why MWNTs are easier to grow from most hydrocarbons than SWNTs, which can only be grown from selected hydrocarbons (e.g. CO, CH₄, etc., that have a reasonable stability in the temperature range of 900–1200°C). Common efficient precursors of MWNTs (e.g. acetylene, benzene, etc.) are unstable at higher temperatures and lead to the deposition of large amounts of carbonaceous compounds other than CNTs.

Transition metals (Fe, Co, Ni) are the most commonly used catalysts for CNT growth, since the phase diagram of carbon and these metals suggests finite solubility of carbon in these transition metals at high temperatures. This leads to the formation of CNTs under the growth mechanism outlined above. Solid organometallocenes (ferrocene, cobaltocene, nickelocene) are widely used as catalyst materials because they liberate metal particles in situ that efficiently catalyze CNT growth. The catalyst particle size has been found to dictate the tube diameter. Hence, metal nanoparticles of controlled size can be used to grow CNTs of controlled diameter²⁹. Thin films of catalyst coated onto various substrates have also proved successful in achieving uniform CNT deposits³⁰. In addition, the material, morphology, and textural properties of the substrate greatly affect the yield and quality of the resulting CNTs. Zeolite supports with
catalysts in their nanopores have resulted in significantly higher yields of CNTs with a narrow diameter distribution\textsuperscript{81}. Alumina materials are reported to be better catalyst supports than silica owing to their strong metal-support interaction, which allows high metal dispersion and, thus, a high density of catalytic sites\textsuperscript{82}. Such interactions prevent metal species from aggregating and forming unwanted large clusters that lead to graphite particles or defective MWNTs. The key to obtaining high yields of pure CNTs is achieving hydrocarbon decomposition on catalyst sites alone and avoiding spontaneous pyrolysis. It is remarkable that transition metals have proven to be efficient catalysts not only in CVD but also in arc-discharge and laser methods. This indicates that these apparently different methods might have a common growth mechanism for CNTs, which is not yet clear.

CNTs have been successfully synthesized using organometallic compounds (nickel phthalocyanine\textsuperscript{83} and ferrocene\textsuperscript{84}) as carbon-cum-catalyst precursors, though the as-grown CNTs were mostly metal encapsulated. The use of ethanol has drawn attention for synthesizing SWNTs at relatively low temperatures (~850°C) on Fe-Co impregnated zeolite supports and Mo-Co coated quartz substrates\textsuperscript{85-87}. Recently, a tree product, camphor, has been used to produce high yields of high-purity MWNTs\textsuperscript{88-90}. Because of the low catalyst requirement with camphor, as-grown MWNTs are the least contaminated with metal, while the oxygen atoms present in camphor help oxidize amorphous carbon in situ\textsuperscript{91}. Fig. 6c shows an SWNT and MWNT grown from camphor.

CVD is ideally suited to growing aligned CNTs on desired substrates for specific applications, which is not feasible by arc or laser methods. Li et al.\textsuperscript{92} have grown dense MWNT arrays on Fe-impregnated mesoporous silica prepared by a sol-gel process, Terrones et al.\textsuperscript{93} have produced CNTs on Co-coated quartz substrates via CVD of a triazene compound with nearly no byproducts, while Pan et al.\textsuperscript{94} have reported the growth of aligned CNTs of more than 2 mm in length over mesoporous substrates from acetylene. Highly aligned nanotubes for electronics have been grown from acetylene\textsuperscript{95} using a Co catalyst impregnated in alumina nanochannels at 650°C, while pillars of parallel CNTs have been grown from ethylene on Fe-patterned Si plates at 700°C for field emission applications\textsuperscript{80}. Bearing in mind that pyrolysis of a xylene-ferrocene mixture leads to the growth of vertical CNTs on quartz\textsuperscript{96}, Ajayan and coworkers have produced organized assemblies of CNTs on thermally oxidized Si wafers\textsuperscript{97,98}, since CVD is a well known and well established industrial process, CNT production is easy to scale up. MWNTs of controlled diameter are being produced in large quantities (~100 g/day) from acetylene using nanoporous materials as the catalyst support\textsuperscript{99}. Wang et al.\textsuperscript{100} have developed a nano-agglomerate fluidized-bed reactor (a quartz cylinder 1 m long and 0.25 m wide) in which the continuous decomposition of ethylene gas on an Fe/alumina catalyst at 700°C produces a few kilograms of MWNTs per hour with a reported purity of 70%. Dai’s group has scaled up SWNT production from methane using a Fe-Mo bimetallic catalyst supported on a sol-gel derived alumina-silica multicomponent material\textsuperscript{101}. However, Smalley’s lab still leads the way in the mass production of SWNTs (~10 g/day) by the high pressure carbon monoxide (HiPco) technique\textsuperscript{102}. In this method, a Fe pentacarbonyl catalyst liberates Fe particles in situ at high temperatures, while a high pressure of CO (~30 atm) enhances the carbon feedstock manifolds, which significantly speeds up the disproportionation of CO molecules into carbon atoms and accelerates SWNT growth.

Apart from large-scale production, CVD also offers the possibility of growing single nanotubes for use as probe tips in atomic force microscopes (AFM) or as field emitters in electron microscopes. Hafner et al.\textsuperscript{103} have grown single SWNTs and MWNTs (1-3 nm in diameter) rooted in the pores of Si tips suitable for AFM imaging. In another approach, single SWNTs are grown directly onto pyramids of Si cantilever-tip assemblies\textsuperscript{104}. In this case, a SWNT grown on the Si surface (controlled by the catalyst density on the surface) protrudes from the apex of the pyramid. As-grown CNT tips are smaller than mechanically assembled nanotube tips by a factor of three and enable significantly improved resolution. CVD-produced CNTs have great promise for the fabrication of sophisticated instruments and nanodevices.

**Concluding remarks**

We have seen here that each method has its own merits and limitations. Overwhelming research is going on around the world to solve the problems involved and understand this ‘nano world’. We have presented only a glimpse of the journey that nanotubes have taken over the last 13 years, though we sincerely feel that each day of this journey has been interesting, inspiring, and challenging. The journey through this long, narrow tunnel continues, with more dramatic turns, surprising scenes, and exciting events still ahead. MT