

PRESENT AND FUTURE WITH CARBON NANOTUBES

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Keywords: Carbon nanotubes, single-wall nanotubes, multi-wall nanotubes, applications

Abstract: Carbon nanotubes (CNTs) are supposed to be a key component of nanotechnology. Carbon nanotubes include both single and multi-walled structures. Almost every week a new potential application of CNTs is identified, stimulating scientists to peep into this tiny tube with ever increasing curiosity. With one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper. However a carbon nanotube promises the greatest variety of applications.

1. Introduction

Carbon nanotubes (CNTs) are a fascinating subject for curiosity-driven research. Carbon nanotubes include both single and multi-walled structures. CNTs are rolled up sheets of sp^2 bonded graphite with no surface broken bonds. Their possible applications arise from the remarkable properties of single-walled nanotubes (SWNTs) such as the highest Young's modulus, highest thermal conductivity, ballistic electron transport, and high aspect ratio structure [1].

There are many other types of nanotubes, from various inorganic kinds, such as those made from boron nitride, to organic ones, such as those made from self assembling cyclic peptides consisting of protein components or from naturally occurring heat shock protein which are extracted from bacteria that thrive in extreme environment. However a carbon nanotube promises the greatest variety of applications [2].

A carbonaceous nanotube has a hollow part with an inner diameter of, at most, 5 nm, and a thickness part of, at most, 10 nm. The thickness part is formed of carbon atoms and hydrogen atoms, optionally containing at least one transition metal atom. Such a carbonaceous nanotube has excellent conductivity and excellent wettability.

Nanotubes are produced by three methods: laser furnace, the arc, and chemical vapor deposition (CVD). Laser methods are not for large-scale production. The problem with arc material is purification. Removal of non-nanotube carbon and metal catalyst material is much more costly than production itself. In addition, there is no simple, routine method to measure purity. Electron microscopy is too costly, Raman spectroscopy sees mainly the nanotubes because of their huge cross-section, so infrared may be the eventual method³, but no standards have been agreed. CVD is the only truly scalable method, with the advantage that purity can be controlled by careful process control [3].

Nanotube composites have a much better surface finish than the previous carbon black or carbon fiber composites. Another use of nanotube composites is as antistatic shielding, on airplane wings and fuselages for example. This is a realistic application. A future use is for shielding of electromagnetic interference, a critical application for many industrial sectors. This would require a composite with conductivity of 1 S·cm. This requires that the

carbon phase should be highly conducting and is probably only achievable if SWNTs are used as the loading. It is achievable, however, and is a credible application.

A fourth application of conducting composites is as a transparent conductor. There is a huge market for transparent electronic conductors such as indium tin oxide (ITO) in displays. In this field, there is a drive towards flexible displays on plastic substrates. ITO is less good for this situation as it is brittle and has poor adhesion to plastic. Conducting composites of SWNTs can be transparent if thin enough [4].

2. Single-wall carbon nanotubes (SWCNTs) and multiwalled nanotubes (MWCNTs)

Carbon nanotubes include both single and multi-walled structures. Single-wall carbon nanotubes (SWCNTs) comprise a cylindrical graphite sheet of nanoscale diameter capped by hemispherical ends. The closure of the cylinder is result of pentagon inclusion in the hexagonal carbon network of the nanotube walls during the growth process as shown in Fig.1, they have diameters typically $\sim 1\text{nm}$. The multi-walled nanotubes (MWCNTs) comprise several to tens of incommensurate concentric cylinders of these graphitic shells with a layer spacing of spacing 3.4\AA as as shown in Fig. 2, WCNTs tends to have diameters in the range 2-100nm,with 10-20nm being typical, and 2- 10nm internal diameter [5].

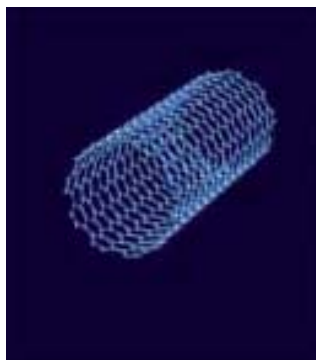


Fig: 1 Single-walled carbon nanotubes

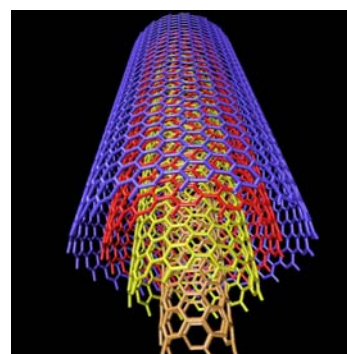


Fig. 2 Multi-walled carbon nanotubes [5].

The smallest diameter reported to date is 40\AA , this corresponds to the predicted lower limit for stable SWCNT formation from consideration of the stress energy built into the cylindrical structure.

3. Production of carbon nanotubes

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3.1. The arc-discharge method

The arc-discharge method is the one by which carbon nanotubes were first produced and recognized. The evaporation of graphite rods in contact by applying an ac voltage in an inert gas to produce fullerenes was carried out. This method creates nanotubes through arc-vaporization of two graphite rod placed end to end, separated by approximately 1mm, in an

enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). After applying a dc arc voltage between two separated graphite rods by modifying 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 [6].

The diagram leading to carbon nanotube production is as shown in Fig. 3, an appropriate ambient gas is introduced at the desired pressure after evacuating the chamber with a vacuum pump and then a dc arc voltage is applied between the two graphite rods.

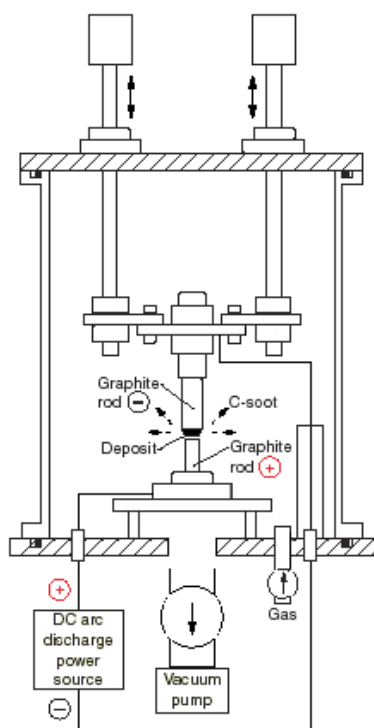


Fig. 3 The arc-discharge method [6]

The anode evaporates to form fullerenes, which are deposited in the form of soot in the chamber as the pure graphite rods are used. A small part of the evaporated anode is deposited on the cathode, which includes CNTs. These CNTs, made of coaxial graphene sheets are found not only on the top surface of the cathode deposit but also deep inside the deposit.

Large-scale synthesis of MWCNTs by arc discharge has been achieved by using He-gas, and their thermal purification has also been successful. When a graphite rod with metal catalyst (Fe, Co, etc.) is used as the anode with a pure graphite cathode, (SWCNTs) are generated in the form of soot. The crystallinity and perfection of arc-produced CNTs are generally high, and the yield per unit time is also higher.

When a graphite rod containing metal catalyst (Fe, Co, etc.) is used as the anode with a pure graphite cathode, single-walled carbon nanotubes (SWCNTs) are generated in the form of soot.

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:



Therefore, pure graphite rods were arc evaporated in pure hydrogen gas [7]. 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.

3.2. Laser-furnace method

The laser furnace method had been originally used as a source of clusters and ultrafine particles was developed for fullerene and CNT_s production. The laser vaporization method is widely used for the production of SWCNTs. The laser is suitable for materials with a high boiling temperature such as carbon as the energy density of lasers is much higher than that of other vaporization devices.

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. 4 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 [8].

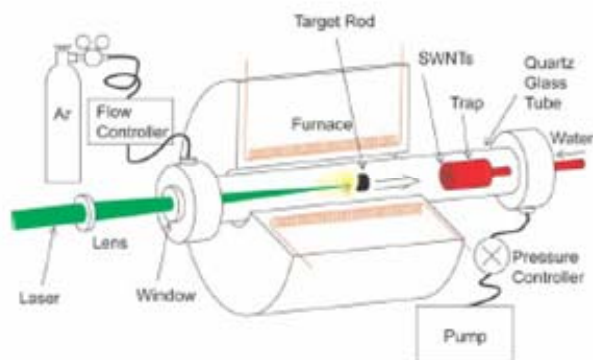


Fig.4 Schematic diagram of the laser-furnace apparatus [8].

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 cm³•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 [9].

3.3 Chemical vapor deposition (CVD)

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. Fig. 3.1 shows a diagram of the setup used for CNT growth.

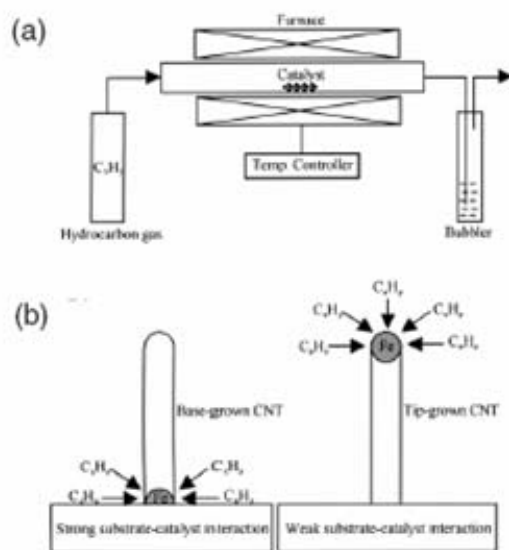


Fig.5 (a) Schematic diagram of a CVD setup. (b) Probable models for CNTs growth [10].

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 [10].

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.

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. 5 with no dangling bonds and, hence, minimum energy [11].

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).

Conclusions

Researchers anticipate nanotube applications in several important areas. One use is as field emitters in *flat-panel display technologies*, an application that will probably become available as products sooner than any other. SWCNT displays could eventually displace liquid-crystal and plasma displays in large flat panels.

Another potential application lies in *ultraminiaturized electronics*. Companies have active research programs for investigating usage carbon nanotubes for future generations of nonsilicon microchip circuitry, which could be 0.01% the size of today's most advanced versions, or smaller. Nanotubes can also be used to make *high-performance fibers* with double the energy absorption and increased tensile strength, and for efficient, flexible, low-cost sensors for gas-leak detection, medical monitoring, and industrial process control.

REFERENCES

1. Baughman, R. H., et al., *Science* (2002) 297, 787
2. R. Saito, G. Dresselhaus, *Physical properties of carbon nanotubes*, Imperial College Press, London, 1998.
2. Nilesh V., S. Ojha, *Potential Future with carbon nanotubes*, Matunga, Mubai, India, (2002)
3. Yoshinori A. Xinluo Z., *Growing carbon nanotubes*, *Material Today*, 25 (2004), 41-52
4. Haddon, R. C., et al., *MRS Bulletin*. (2004) 29, 252
5. Peter J. F. Harris, "*Carbon Nanotubes and Related Structures*", (1999), 3
6. Wang, N, Tang, Z.K., Li., G. D., and Chen, J, S., *Nature*, (2000), 408, 50-51
7. Ebbesen, T. W., and Ajayan, P. M., *Nature* 1992358, 220
8. Hirahara, K., et al., *Phys. Rev. Lett.* (2000) 85, 5384,
9. Shimada, T., et al., *Appl. Phys. Lett.* (2004) 84 (13), 2412
10. Dresselhaus, M. S., et al., (1988) *Graphite fibers and filaments*, Springer, Berlin
11. Baker, R. T. K. In *Chemistry and Physics of Carbon*, Dekker, New York, 197814