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Trends in the Development of Carbon Nanotube Production Technology

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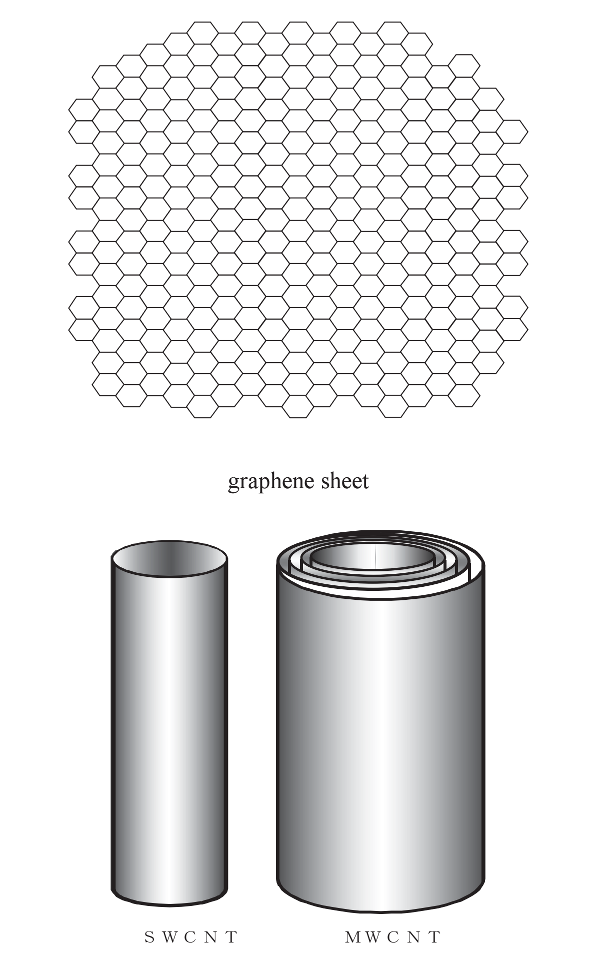
8.1 Introduction

The carbon nanotube (CNT) is a cylindrical material formed by rolling up a sheet of graphite monolayer, made up of a series of six-membered carbon rings linked together (graphene sheet), having a diameter between about 1 nm and several tens nm and a length of about 1 μm. There are two kinds of CNTs: the single-walled CNT (SWCNT) consisting of one layer of carbon atoms; and, the multi-walled CNT (MWCNT) made up of layers of concentric hollow cylinders (see Chart 1). The MWCNT was the first CNT found by Iijima of NEC in 1991, and then the SWCNT was simultaneously reported on by the NEC group and IBM group in 1993.

Chart 1: Schematic diagrams of graphene sheet, SWCNT, and MWCNT.



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Recently, it has been made clear that CNTs have various unique characteristics. Among them are: i) shape (diameter at the tip is small and the aspect ratio is large); ii) electronic properties (sometimes metallic and sometimes semiconducting depending on the way the graphene sheet is rolled up and the tube diameter, resonance tunnel effect, transistor characteristics by the electric field effect, etc.); iii) adsorption characteristic; and, iv) excellent mechanical properties. Making use of these characteristics, many possibilities for application are expected. In this paper, recent trends in developing production technology for CNT, which is the key to putting this excellent material to practical use, are mainly explained.

8.2 Expected applications for CNT, and the necessity of the development of production technology

8.2.1 Expected applications for CNT

Reflecting the progress of application development for CNTs, the number of patent applications has been drastically increasing recently. Chart 2 shows the change in the number of published patent applications in Japan by years, which shows that many ideas have been proposed

relating to the application of CNTs. Chart 3 shows examples of expected applications for CNTs.
Among these possible applications, SPM probes have been put to practical use (MWCNTs for SPM probes have been on the market since 2000), and trial products of FED using CNTs as the emitter have been introduced by Ise Electronics Corporation, Samsung of Korea, and NEC.

8.2.2 Necessity to develop the production technology for CNTs

While intensive research is being made on the development of applications for CNTs as described above, at present, they can be produced only in the order of grams per day and the price is as high as about ¥10,000 per gram. When CNTs are put to practical use, however, particularly for the emitter of field-emission display(FED), hydrogen absorbing material, negative electrodes for lithium secondary batteris, and composite material among the above-mentioned applications, the quantity required is very large and, at the same time, the price is required to be low. In order to promote the practical applications of CNTs, it is indispensable to develop the technology to produce CNTs in a large amount such as several kilograms a day at low cost.
As described above, there are two kinds of CNTs: MWCNT and SWCNT, and even for the same kind of CNTs properties vary depending on the tube diameter, etc. It is said that MWCNTs are suited for the emitter of FED and composite material, whereas SWCNTs are suited for hydrogen absorbing material and electrodes for lithium secondary batteries. So it is necessary to produce different kinds of CNT according to the intended applications.

8.3 Outline of typical methods to synthesize CNTs.

In general, CNTs are synthesized by placing carbon or carbon-containing material in a high-temperature environment under the presence of catalysts. Outline and features of major synthesizing methods are as follows.

(1) Arc discharge method

When an arc of about 20V and 50A is discharged between carbon rods in an atmosphere of argon or hydrogen at a pressure a little lower than the atmospheric pressure, MWCNTs are produced in the deposit on the negative electrode. Furthermore, when catalysts such as nickel or cobalt are added to the carbon rods and the arc is discharged, SWCNTs are produced in the soot

Chart 2: Number of patent gazettes (unexamined patent application) relating to CNT

Year of publication	Number of patent gazettes
1994	9
1995	12
1996	10
1997	3
1998	11
1999	36
2000	57
2001 (until May)	42

Retrieved from the Japan Patent Office Database using "carbon nanotube" as the keywords.

Chart 3: Examples of expected applications for CNT

Application	Advantage of CNT	Status of development
Probe for scanning probe microscope (SPM)	Many advantages including the possibility of observing very fine structures.	In practical use
Emitter for field-emission display (FED)	Low power consumption of a light emitting display is possible.	Trial production stage
Hydrogen absorbing material	Hydrogen absorbing material for fuel cells having a high hydrogen absorbing capacity.	Under basic research
Negative electrodes for lithium secondary batteries	Material for negative electrode having larger capacity than conventional materials.	Under basic research
Field-effect transistor	Significant densification of integrated circuits and other mprovements are possible.	Under basic research
Composite material	Reinforcement and conductivity are provided to high-performance plastics.	Under application development

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deposited inside the vessel. Whereas high-quality CNTs with few defects are obtained by the arc discharge method, it will be difficult to produce large amounts.

(2) Laser ablation method

When intense laser pulses generated by YAG are radiated at carbon mixed with catalysts such as nickel or cobalt, SWCNTs are produced. In this method, relatively high-purity SWCNTs are obtained and it is also possible to control the diameter of the nanotubes by varying the conditions. Since the yield is low, however this method will not be suitable for the industrial production of CNTs.

(3) Chemical vapor deposition method (CVD)

CNTs are obtained by bringing carbon compounds, as the carbon source, into contact with catalysts of fine metallic particles at 500 to 1000 ℃. Properties of CNTs vary depending on the kind and arrangement of catalysts, and either MWCNTs or SWCNTs can be synthesized depending on the conditions. It is also possible to produce CNTs oriented in the perpendicular direction to the substrate by the arranging of catalysts on it.

Because the raw material can be supplied as a gas, this method is considered to be suitable for mass synthesizing, but CNTs synthesized by this method, in general, have many defects.

Among the above-mentioned methods, CVD is suitable for large amount production, and the arc discharge method is suited for small-scale production of nanotubes with less defects. Application of the laser evaporation method seems to be limited to research purposes to elucidate the mechanism of CNT generation.

8.4 Situation of production technology development in Japan

Relating to the technologies for producing CNTs in large quantities, the status of development of the CVD process, which is considered to be suitable for mass production, is explained first; then the status of the arc discharge method, which provides CNTs with less defects, is explained; and, other newly proposed methods are explained lastly.

8.4.1 CVD method

Development of the CVD method, which is considered to be suitable for mass synthesis, is progressing. Two examples, fluidized catalyst method, test plants of which are being operated and a method using catalysts supported on zeolite, are as explained below.

(1) Fluidized catalyst method

Dr. Yumura, a leader of the National Institute of Materials and Chemical Research (now reorganized as the Research Center for Advanced Carbon Materials, National Institute of Advanced Industrial Science and Technology), and his co-workers applied the synthesizing process for carbon fibers using chemical vapor deposition originally developed by Professor Endo of Shinshu University. In this process, instead of placing fine catalyst particles on the substrate beforehand, fine catalyst particles or catalyst precursors that convert to fine catalyst particles under the CVD conditions are dispersed in the raw material hydrocarbon (such as benzene or toluene), and the mixture is transferred into a reactor heated to about 1000 ℃ together with hydrogen to obtain MWCNTs. Iron, cobalt, nickel, etc., are used as the catalyst. The resulting product is heated to 1200 ℃ to remove tar content in the CNTs, and then heated to a high temperature of 2000 ℃ to convert the portion that is not fully graphitized to graphite.

A pilot plant adopting this process has been built by Showa Denko K.K., and production conditions are being studied. They have announced that they achieved a production capacity of about 200g/hr (corresponding to several kilograms per day), and the plant is the first in the world to reach this production capacity.

(2) Method using catalysts supported on zeolite

Professor Shinohara of Nagoya University and his colleagues reported that CNTs with less impurities were obtained by bringing a gas mixture of acetylene and argon into contact at 600 to 900 ℃ with catalyst powders prepared by placing iron/cobalt on Y-type zeolite, which is a kind of porous silicate. According to the report, it is possible to produce either SWCNTs or MWCNTs by changing the contacting conditions, and to vary the shape of CNTs by changing the type of zeolite. Zeolite and CNTs are separated by dissolving zeolite with hydrofluoric acid.

Professor Shinohara and his colleagues consider that this method can be easily scaled up, and intend to make a study on such scale-up in the future.

8.4.2 Arc discharge method

While the arc discharge method provides high-quality CNTs with less defects, it has been considered that scaling-up is difficult. However, a new situation has emerged recently. Associate professor Takigawa of Toyohashi University of Technology found a method by which CNTs can be synthesized under atmospheric conditions without requiring a special reactor. Associate professor Takigawa considers that it is possible to construct a mass-production process by applying this method, and future development is expected.

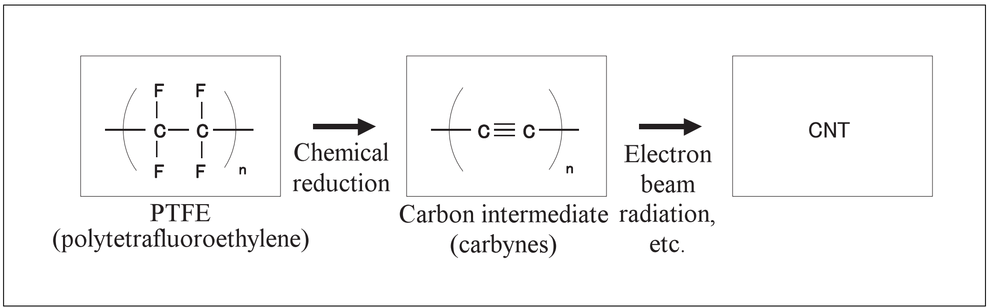
8.4.3 Other methods

Completely new and original methods have been proposed aiming at mass-production, and two of them are introduced below.

(1) Method using carbynes as the carbon source

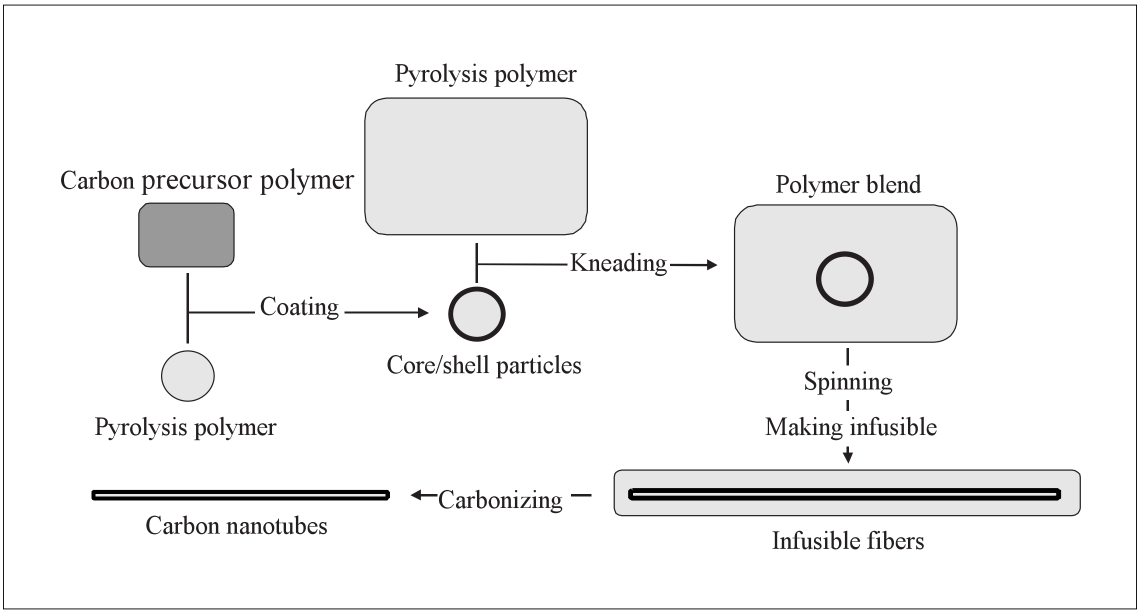
This method was developed by Osaka Gas Co. In this method, carbynes are produced by reducing polytetrafluoroethylene with magnesium, and then CNTs can be synthesized by radiating the carbynes with electron beams, etc. (see Chart 4). It is stated that CNTs are synthesized under relatively moderate conditions and that the method is also superior to other conventional

Chart 4: Method using carbynes as the carbon source



Prepared by the Science and Technology Foresight Center based on data provided by Osaka Gas Co.

Chart 5: Method by carbonizing carbon precursors of polymer tubes



Prepared by the Science and Technology Foresight Center based on data provided by the Otani Laboratory of Gunma University.

methods in mass-production capability.

(2) Carbonization of carbon precursors of polymer tubes

Core/shell particles consisting of a shell of carbon precursor polymer (such as polyacylonitrile) and a core of pyrolysis polymer (polyethylene) are dispersed in pyrolysis polymer. The core/shell particles are elongated into a rod shape by the melt-spinning of this mixture. Then CNTs are obtained through making infusible and carbonization. This unique method has been proposed by Professor Otani of Gunma University (see Chart 5).

Professor Otani considers that this method is suitable for mass production because the method's production conditions are similar to those for conventional carbon fiber production.

8.5 Overseas situation

Basic and application research relating to CNT is progressing in the United States, and several U.S. venture firms have proposed CNT synthesis methods.

Hyperion Catalysis patented a method to synthesize CNTs by the CVD process using catalysts of iron, etc., but their present development status is unknown. A venture business founded by Professor Richard Smalley, who was recently granted the Nobel Prize for his work in fullerene, and his co-workers at Rice University announced that they were planning to build a pilot plant for producing SWCNTs, with a production capacity in the order of kilograms per day, by bringing carbon monoxide into contact with catalysts under high temperature and high pressure. Incidentally, production technology for SWCNTs has not been developed in Japan.

8.6 Conclusion

The CNT that was found in Japan is expected to be used for various applications due to its unique nano-material characteristics. For the future development of CNT applications, the production technology is one of the most important factors.

At present, Showa Denko K.K. is the only one planning to synthesize CNT (MWCNTs) at a plant production level of several kilograms per day. They use the fluidized catalyst CVD process, and the quality and cost of the CNT product are now being assessed, with the results awaited.

Several proposals have been made as new synthesis methods aiming at mass production, but they are still at the stage of small-scale laboratory tests. Therefore, it is necessary to assess, by scaling up the equipment, the quality and cost of CNT products and other possibilities of these methods from now. Although it has not been mentioned in this paper, separation and purification technology is another subject of technological development, as CNTs do not dissolve in solvents making them difficult to separate and purify.

Since the properties of CNT vary depending on the diameter and the other factors of nanotubes, it is necessary to control these factors. Relating to this technology, basic studies are now being made in laboratories, but it is not yet possible to control these factors to produce CNTs with the desired properties. Further fundamental research including studies to elucidate the mechanism of CNT generation is required.

In addition, properties required for CNTs differ depending on specific applications. For example, the degree of purity required for the emitter of FED and that for hydrogen absorbing material are different. Attention must be paid to this fact when developing the production technology.

It seems that business corporations are not overly enthusiastic for the development of CNT production technology. The reason is probably because the prospects of demand for CNT is not yet clear, and the research in scaling up the production technology is costly due to its peculiar production conditions. As a result, it seems that the above-mentioned results of basic research conducted at universities and institutes are not properly handed over to business corporations, who are good at putting basic technologies to practical use.

In the USA, as mentioned above, CNT researchers tend to actively establish venture businesses in order to put their results of research to practical use. I believe Japanese researchers should follow such an attitude as in the USA.