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Carbon Nanotube Research: Past and Future*

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In this paper, my experience of over 30 years in carbon materials and carbon nanotube (CNT) researches is reported. Moreover, an overview of the background of the development of CNT synthesis, the present status of CNT science and technology, and the future prospect of CNTs are described.

1. Start from a Paper Published in *Oyo Buturi*

One year after I became a research associate at the Faculty of Engineering of Shinshu University, when I was 26 years old, my first paper was published in *Oyo Buturi*.[1] The paper was on the synthesis and structure of vapor-grown carbon fibers. In the late 1970s, the carbon fibers (CFs), which were called a black revolutionist, attracted much attention as an aerospace-related material, and the competition to develop CFs using organic fibers such as rayon, polyacrylonitrile (PAN), and pitch as precursors (feedstocks) has been intensifying among Japan, the US, and European countries. Carbon science has been accumulating 100 years of research before the big bang of silicon era, the main research interest on carbon materials was on bulk carbon. In those times, the carbon researchers around the world, who prided themselves as a group of specialists with expertise on carbon, were impressed by the fact that CFs have revolutionary mechanical functions as the first one-dimensional system of carbons. The researchers were excited by the performance records rewritten daily. At that time, this newly developed material technology led the science, and the properties of the one-dimensional carbon materials without impurities, such as strength and electronic properties, and its structure stimulated the development of carbon science. Such progress further contributed to the development of technology; it was a period in which an interactive cycle between science and technology was created. The target of my study was, then, to synthesize ideal CFs with superior properties to those obtained by carbonizing organic fibers, directly from the gas phase. What properties or functions can be obtained? How are CFs grown by thermal decomposition of hydrocarbon gas and in what area can the CFs be applied? Even though these demanding themes required much time to attain results, I was willing to put strenuous effort to this challenging research.

Vapor-grown CFs were obtained by the following processes: benzene or methane gas diluted with hydrogen gas was introduced into a reaction tube heated to approximately 1,000 °C for thermal decomposition, so-called pyrolysis, and fibrous carbon with a diameter of 20–30 μm and a maximum length of 2–3 cm were grown on a ceramic substrate. However, there were only several carbon fibers generally up to 1 cm long in the soot deposited on the substrate and also, the reproducibility was poor, which was far from our target.

Under such circumstances, I was granted a fortuitous moment. I was repeating the synthesis experiment in which the soot deposition and thermally decomposed carbon films are baked in air to obtain a cleaned white ceramic substrate again. In order to shorten the experiment time, I brushed the ceramic substrate with sand paper, instead of baking, to remove the carbon deposits and used the still rather blackened substrate again in the experiment. By chance, I used the sand paper normally used for wood working stored at my laboratory. The next morning, when I opened the rubber stoppers of the cooled reaction tube with a diameter of approximately 3 cm, clusters of glossy several-centimeter-long CFs had grown on the ceramic substrate in the reaction tube. Although it was not scientific, I repeated the same processes everyday and found that the reproducibility was surprisingly high. In addition, CFs without contamination of byproducts such as soot were obtained. Subsequently, the ceramic substrate was replaced with an artificial graphite tube polished by the sand paper, and the clarification of the growth phenomena and research on the analysis of the properties of the synthesized CFs headed in the right direction. A paper summarized on the basis of this discovery was published in *Oyo Buturi*.[1] In the paper, I reported that the length of the primary fibers increases up to 60 mm and then the diameter increases to approximately 25 μm with increasing thermal decomposition time by pyrolytic deposition. It was clarified that the vapor-grown CFs are obtained through two growth processes in the length and thickness directions (Fig. 1). The reproducibility of the experiment was maintained, and the thickness of the CFs was controlled; furthermore, ultrafine CF samples with nanometer-scale diameters were synthesized.

2. Going to France to Study High-Resolution Electron Microscopic Analysis and Catalytic Growth Model

At that time, Shinshu University installed scanning electron microscopes (SEM) and X-ray microanalyzers (XMA). Using these systems, I found that the CFs have a cross section resembling the annual ring structure of a tree and that the thickness of the CFs increases as the thermally decomposed carbon layers are deposited on the thin primary fibers. However, it was not possible to elucidate the mechanism underlying the increase in the length of the ultrathin primary fibers using these systems.

After the publication of my paper in *Oyo Buturi*,[1] many researchers expressed interest in my work. One of these researchers included Professor A. Oberlin at the University

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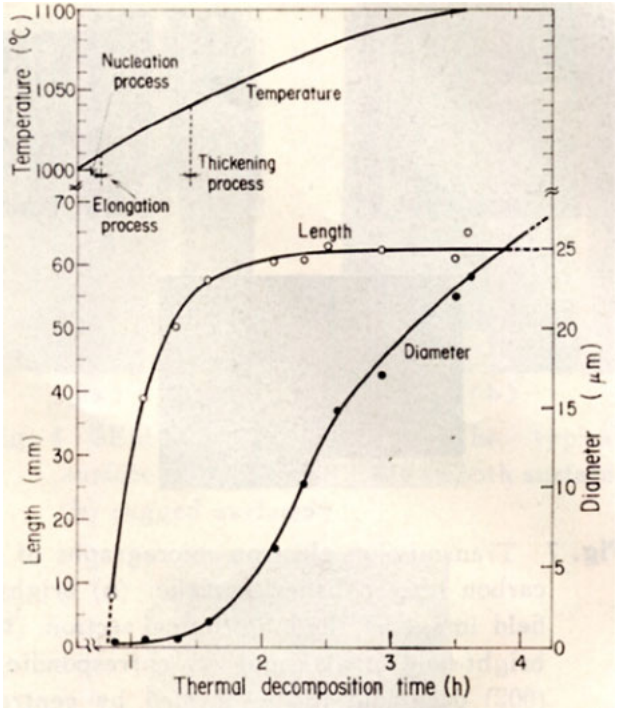

Fig. 1. (Color online) Experimental results demonstrating that vapor-grown CFs are obtained from thin primary fibers through two processes, i.e., growth first in the length direction and then in the thickness direction with increasing thermal decomposition time.[1)]

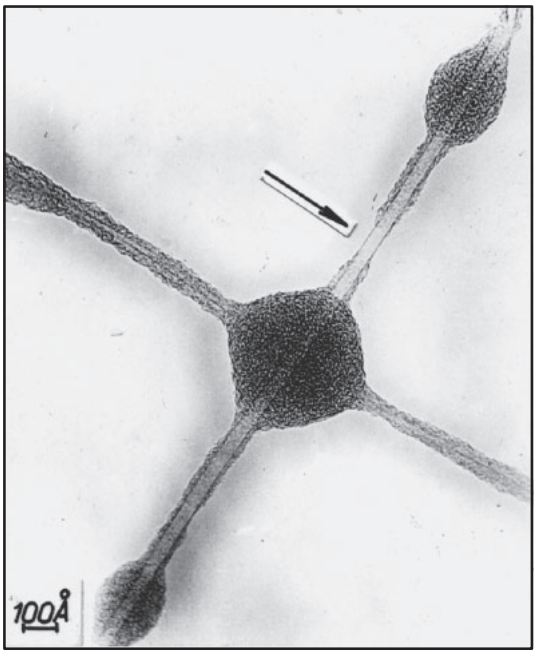

Fig. 2. TEM image showing that long, straight and parallel carbon layers exist at the core regions, and that carbon layers are curled into a cylindrical shape to from a hollow tube. Reprinted from ref. 2 with permission from Elsevier.

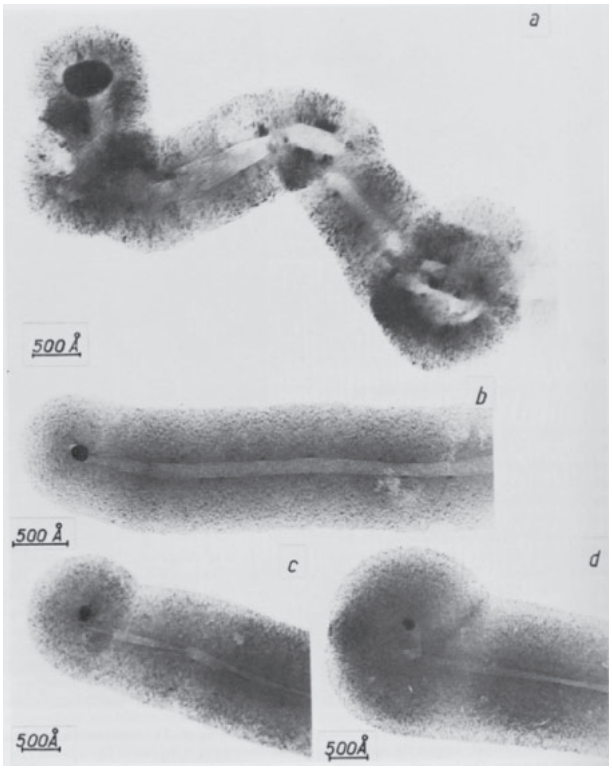

Fig. 3. Nanometer-size iron catalyst particles (iron carbide particles) at the tip of the hollow tube of each fiber. Reprinted from ref. 2 with permission from Elsevier.

of Orleans (France), who is a prominent researcher of carbon by electron microscopic analysis, and I got a chance to study in Orleans (France). Ultra-thin CF samples with a diameter of 100 nm or less were required as samples for transmission electron microscopy, however, the synthesis of such thin CF samples was very easy by using my method. I scraped a large amount of grown CF samples off the substrate using a toothpick to avoid metal contamination and brought them to Laboratoir Marcel Mathieu, CNRS at Orléans (France). Professor A. Oberlin provided thorough instruction on the electron microscopic analysis of carbon, and finally I was conferred full mastership of electron microscopy by Professor A. Oberlin with the complimentary words, "your analytical eye is equivalent and as same as mine". Six months after my visit to France, as I concentrated on electron microscopic analysis in the laboratory during the Christmas holidays in 1975, a chance arose. By then, we found that the thin fibers contain a hollow tube, which was reported in the *Journal of Crystal Growth* published in 1976,[2)] where the wall of the hollow tube is made of long, straight, parallel carbon layers, with each carbon layer being rolled into a cylindrical shape to form a hollow tube (Fig. 2).[2)] This is the same description as for the structure of carbon nanotubes (CNTs). The 1970s was not yet the nanotechnology era, and we described the hollow tube as a "thin primary formed fiber", in the paper, which corresponds to the primary fiber explained in §2. Moreover, I found nanometer-size iron carbide particles (cementite crystals, as in ref. 2) at the tip of the central hollow tube of each fiber (Fig. 3) during the Christmas holidays. The iron carbide catalyst particles are reaction products from iron and iron oxide particles that originated from the brown sand paper that I have mentioned previously. Furthermore, in 1976, our research group proposed a model for the growth of hollow carbon tubes utilizing the catalytic effect of these iron particles (Fig. 4).[2)]

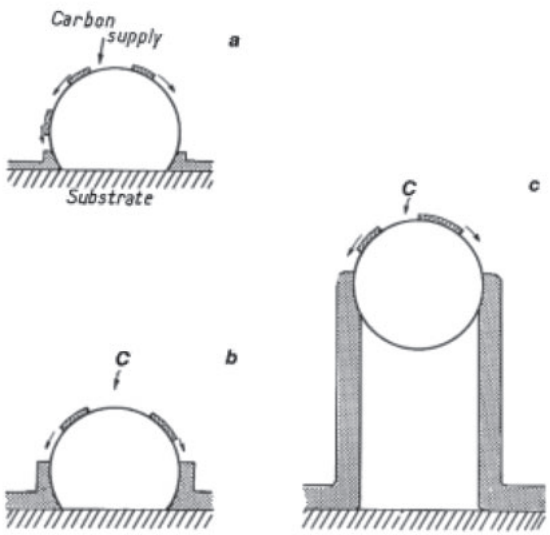

Fig. 4. Growth model of primary grown hollow carbon tube through the catalytic effect of iron particles. Reprinted from ref. 2 with permission from Elsevier.

3. From Science to Invention: Pioneering Mass Synthesis Method and Floating Catalyst Method

After returning to Japan from France, I developed a seeding method (substrate method) based on the growth model proposed in ref. 2, in which nanometer-size iron catalyst particles are dispersed on the substrate to grow CFs. This method enabled the mass synthesis of CFs, sufficient enough to seek real-world applications. In the 1980s, although the price of commercialized PAN-based carbon fibers (CFs) significantly decreased owing to a successful mass fabrication, the production price was still high, which was a major obstacle for researchers. The scientific interest in our CFs with an ideal structure was increasing although innovative mass synthesis methods to decrease the cost were still required. Some leading chemical manufacturers obtained a favorable result by adopting a continuous synthesis method in which substrates with dispersed catalyst particles are continuously transported on a conveyor belt in a reaction furnace. However, the cost of this method was still high.

One morning, as I was searching for a mass synthesis method, I was reading a newspaper on a train on a business trip to Tokyo and found an article on the influenza virus in it. The article reported that viruses can fly off to a distance of 10 m by a sneeze. I flashed on an idea that CNTs might be synthesized by floating the iron particles in a reaction atmosphere, instead of dispersing them onto a substrate, since the size of iron particles used for the synthesis of CNTs is as small as one-thirtieth that of the influenza virus. I immediately tried to apply this idea to the synthesis of CNTs; when introducing a carbon source into a reaction tube with floating catalyst particles, I successfully collected ultrathin, and sponge-like lump samples deposited at the outlet of the reaction tube. This was perhaps my third lucky break in my research career. The thin fibers obtained were the present multiwalled carbon nanotubes (MWCNTs) with a diameter as small as 20–30 nm, a hollow at their centers, and a highly uniform thickness of the fibers. I adjusted the experimental conditions and the result was published in a letter paper in *Oyo Buturi* in 1985.[3)] Moreover, our research group then established a continuous synthesis process of CNTs and received a patent for this technology in 1987.[4)] The technique is called the fluidization method. With this method a mass synthesis process of thin fibers, the present MWCNTs, was established. This achievement was reported in *CHEMTECH* published by ACS Publications in 1988.[5)] At around the same time, the pilot commercial synthesis of MWCNTs started and I was allowed to publish the results (Fig. 5). This patent expired in January 2002.

Currently, it is known that this catalytic chemical vapor deposition (CCVD) method is most commonly used for the synthesis of single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and MWCNTs (Fig. 6).[6,7)] For example, SWCNTs were synthesized by the floating method, and the obtained SWCNTs were directly used to form CNT ropes. In 1988, the industrialization of MWCNTs began experimentally, and the supply of sample MWCNTs began; to this day,

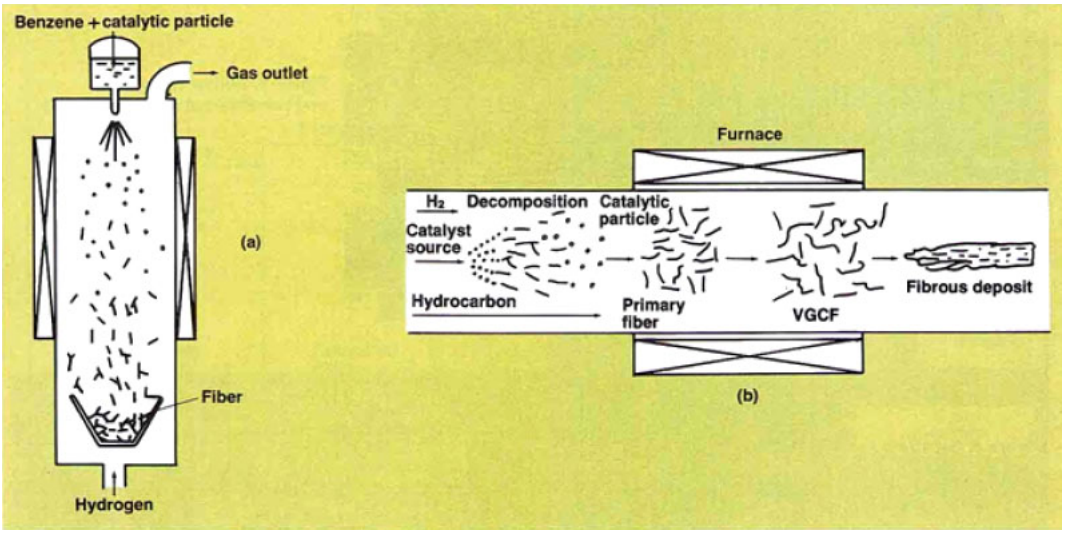

Fig. 5. (Color online) Mass synthesis method of MWCNTs (fluidization method). Reprinted from ref. 5 with permission from American Chemical Society.

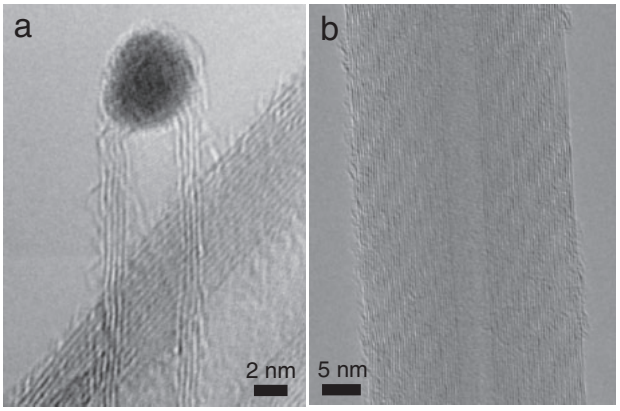

Fig. 6. TEM images of (a) four-walled CNT formed through catalytic effect of iron particles and (b) thermally treated MWCNT.

the most frequently used catalyst in this synthesis method is iron. Now, many production systems for the mass synthesis of MWCNTs by various processes using fluidization CCVD method as a base have been established; MWCNTs have been industrialized in various countries, such as Germany, France, Japan, the US, Belgium, China, the UK and others. Depending on the intended use, there are several types, including as-deposited MWCNTs and those thermally treated at high temperatures (Fig. 6). Since Professor Sumio Iijima published his famous paper on CNTs in 1991,[8] fundamental and application research and the development of CNTs, including single-, double-, and multi-walled structure, have been accelerated, making CFs a material that leads the nanotechnology era within the background of worldwide interest in nanotechnology. *Nature* reported that the global carbon-nanotube revenue in 2009 was approximately 100 million US dollars and expected to approximately 500 million US dollars in 2015.[9] The number of CNT-related papers on fundamental as well as application research has been increasing, indicating that balanced research between fundamental and applied sciences for CNTs has been developed.[10] The continuing support to fundamental research in various fields will be necessary for a stable and substantial development of CNTs.

4. To the Synthesis of DWCNTs

The important factor required for CNTs as a nanotechnology material is precise growth control of structures suitable for the required functions. By using CCVD method, the number of layers, such as single, double, and multiwalled, as described above, can be controlled; we have succeeded in the synthesis of high-purity DWCNTs with high structural perfection by the seeding method using an iron catalyst, that is, the CCVD method. Other major methods reported for DWCNT synthesis include high-temperature pulsed arc discharge[11] and thermal treatment of peapods, i.e., fullerenes encapsulated in SWCNTs.[12] Mainly iron and cobalt particles, as well as molybdenum alloy particles, are used as catalysts in CCVD method, and in these methods, catalyst particle size is precisely controlled on alumina and zeolite supports. We developed a synthesis method of DWCNTs in which the synthesis temperature and also catalyst particle size in particular were optimized using magnesium-oxide and iron catalysts [Fig. 7(a)].[13] It is worthwhile to note that the high-purity DWCNTs had a small diameter almost equivalent to that of SWCNTs, with a narrow diameter distribution. Furthermore, we could fabricate paper-like DWCNTs with high flexibility.[13] By thinning this DWCNT paper, the fabrication of a conductive transparent film is possible,[14] and the application of the film as a transparent and conductive film is expected. Also, DWCNTs have interesting adsorption characteristics; hydrogen is well adsorbed in nanospaces of DWCNTs as in ref 15. Because the diameter of DWCNTs is approximately 1 nm, which is comparable to that of SWCNTs, it is expected that DWCNTs with properties arising from the double-wall structure will be applied to electronic and energy device applications. It is even possible to form a hybrid double-wall structure with only the electronic property of the outer tube changed to the insulator, by fluorinating the outer tube of the coaxial double-wall yet maintaining the intrinsic physical and chemical properties of the inner tube [Fig. 7(b)].[16] Figure 8(a) shows a TEM image of a DWCNT with a fluorinated outer tube. As shown in the figure, the shape of the DWCNT was unchanged by fluorination; the shape of the coaxial double-wall structure remains the same. From the Raman spectra acquired with three different laser lines (532, 633, and 785 nm), the Raman radial breathing mode (RBM), which is a vibration mode in the radial direction unique to CNTs, is selectively suppressed in the outer tube ($< 200\,\mathrm{cm}^{-1}$) owing to fluorination. On the other hand, it is maintained in the inner tube ($> 200\,\mathrm{cm}^{-1}$) [Fig. 8(b)]. It is possible to observe the distribution of the chirality (geometrical helical structure) of semiconducting CNTs by photoluminescence (PL) measurement of DWCNTs. It is well known that SWCNTs become a metal or a semiconductor depending on the chirality, and Fig. 7(c) shows the PL map for pristine DWCNTs (without fluorination). The map shows the distribution of chirality of the inner tube of DWCNTs; three strong PL peaks were ascribed to the inner tubes with chiralities (7, 6), (8, 4), and (7, 5). In contrast, Fig. 7(d) shows the photoluminescence map for fluorinated DWCNTs where the disappearance of signals corresponding to some chiralities is observed after fluorination. On the basis of this finding, it was concluded that the electronic states of the inner tube are unaffected by fluorination of the outer tube, indicating that the electronic states of only the outer tube are selectively changed by fluorination. Namely, even when functionalization, such as the modification of a DWCNT with functional groups and the adhesion of metal catalysts, is carried out on the outer tube, the effects of functionalization on the structure and properties of the inner tube are very limited. An ideal property can be maintained in the inner tube because of the double-wall structure with high structural perfection, which is an advantage of DWCNTs when they are applied as a material in electronic devices and sensors, and as a composite material. This could be called as "DWCNT chemistry".

Due to their unique characteristic, i.e., the presence of a hollow core, DWCNTs have been considered as templates for metal nanowires, and the encapsulation of lanthanum (La)[17] and gadolinium (Gd)[18] atoms has already been reported. We produced nanowires by one-dimensional alignment of molybdenum (Mo) and platinum (Pt) atoms

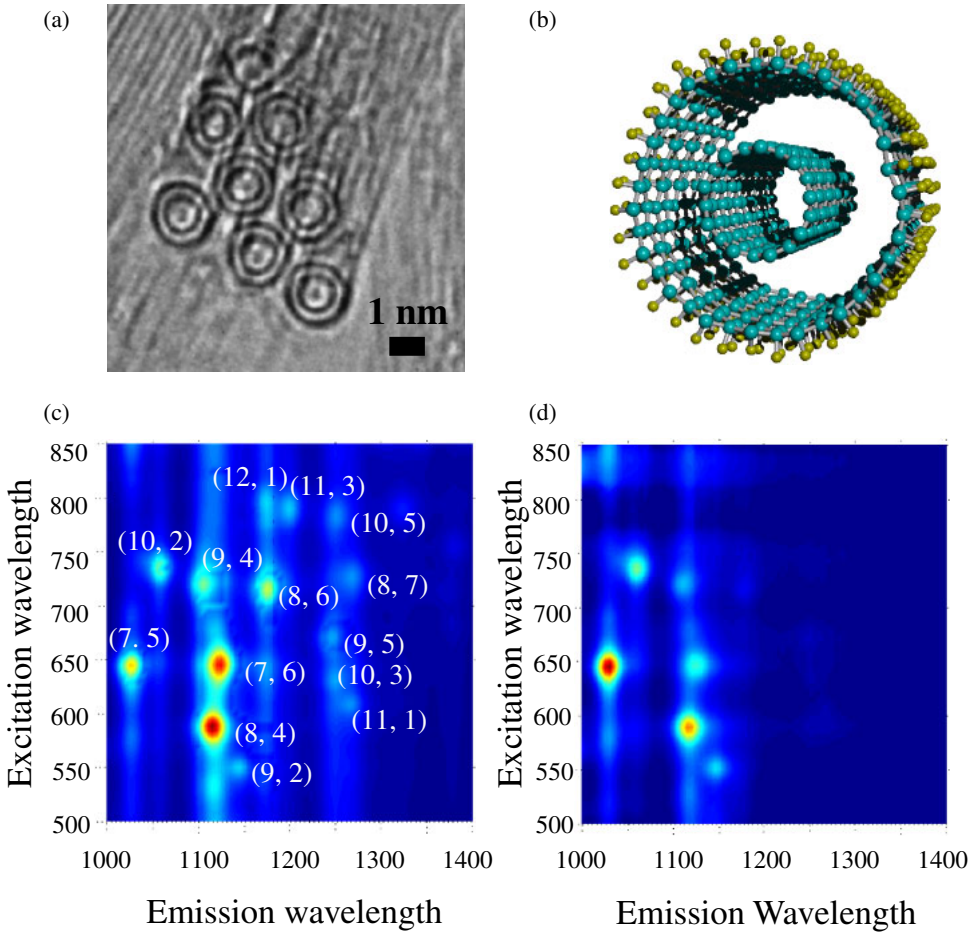

Fig. 7. (Color online) (a) TEM image of DWCNT and (c) its photoluminescence map; (b) structural model of fluorinated DWCNT and (d) its photoluminescence map. Reprinted from ref. 16 with permission from American Chemical Society.

inside the DWCNTs,[19] aiming at the use of these atoms as new catalysts (Fig. 9). In particular, a unique application of DWCNTs, in which the outer and inner tubes have different functions, is expected; for example, the outer tube may be modified with functional groups to add functions and the inner tube with high structural perfection may be used as a conductive or semiconductive SWCNT. In the future, the exploration of methods of mass-synthesizing high-purity DWCNTs by the floating method and the development of their unique applications are expected. The research achievement on DWCNTs by Shinohara *et al.*[11] is noteworthy and the research on DWCNTs is one of the scientific fields in which Japan has been taking a leading role in the world.

5. Development of MWCNT Applications

The CNTs were firstly practically applied to use their mechanical properties. Even when CNTs are subjected to a kneading process with a matrix, the tube shape is maintained, which was not the case for the conventional CFs. Therefore, it is possible to add mechanical, electrical, and thermal conductive functions that are derived from a thin laminated graphene cylindrical structure with high structural perfection to various composite materials.

MWCNTs have been practically used as an electrode additive in lithium-ion batteries (LIBs) since early on in their development, and have accumulated market achievements.[20] An MWCNT electrode additive has contributed to the improvement of the performance of the LIBs and great expectations are placed on plug-in hybrid cars and electric vehicles equipped with LIBs. Figure 10 shows a SEM image of LIB anode graphite to which MWCNTs have been added and are uniformly distributed among graphite particles.[20] Depending on the proportion of MWCNTs added to the LIB anode graphite, the cycle life, namely the cyclability, of the battery is significantly improved; the cycle life increases with increasing proportion of MWCNTs.[20] This improvement is considered to be due to the formation of a flexible conductive network between particles owing to the highest resiliency of MWCNTs resulting from their carbon nanostructure among various materials. Also, it is expected that the addition of CNTs will enhance the electrochemical performance of the LIB, such as rate capability. MWCNTs can also be used as the additive to the cathode of LIBs; the practical application of MWCNTs in this field is already under way. The contribution and application ranges of MWCNTs in power sources other than LIBs for portable electronic devices have been increasing. The use of MWCNTs in lead-acid batteries and electric double-layer capacitors is also strongly expected.

The applications of composite materials of various matrix resins, rubber, and metals using MWCNTs as a filler are being developed. The research on the practical use of MWCNTs such as for containers used in semiconductor

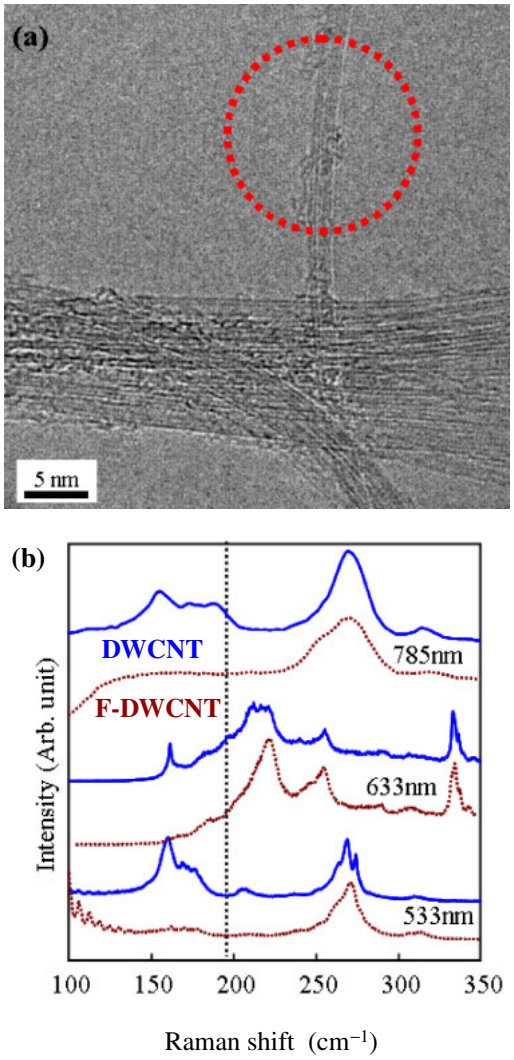

Fig. 8. (Color online) (a) TEM image of fluorinated DWCNT and (b) Raman spectra of pristine and fluorinated DWCNTs. Reprinted from ref. 16 with permission from American Chemical Society.

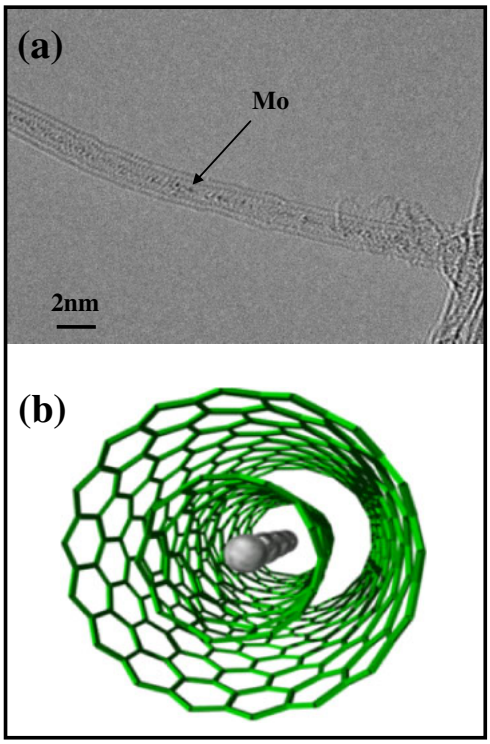

Fig. 9. (Color online) (a) Encapsulation of Mo atoms inside DWCNT and (b) its structural model. Reprinted from ref. 19 with permission from American Chemical Society.

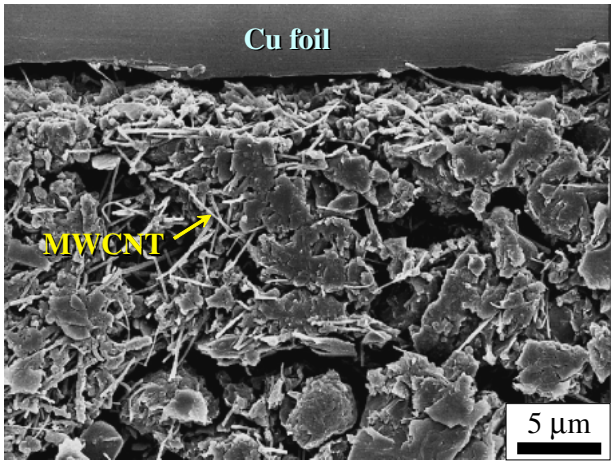

Fig. 10. (Color online) SEM image of LIB anode to which MWCNTs synthesized by CCVD were added. Reprinted from ref. 20 with permission from Elsevier.

fabrication, automobile parts, and windmills for wind power generation has been active, and MWCNTs are expected to add new functions as the third additive for the PAN-based CF composite material, in order to strengthen such as compressive strength. In addition, the composite of MWCNTs with aluminum is applied to a plate with high thermal conductivity. SWCNTs and MWCNTs are expected to have a high thermal conductivity of 3,000–6,000 W/mK at room temperature, which may open up new applications in the fields of metal composite materials used for electronic devices and the cooling of laser elements. The low strength and low corrosion resistance of a normal Mg alloy were improved by the addition of MWCNTs as composite.[21] Owing to this, an advanced composite metal with a light weight comparable to that of plastics can be expected.

The technologies for oil development and exploration are used under harsh conditions; the temperature and pressure of oil wells are as high as 175 °C and 140 MPa, respectively. That pressure corresponds to the hydraulic pressure in the sea at a depth of 14,000 m. An innovative improvement of rubber functions was achieved through the use of a CNT composite rubber, as realized by the cellulated structure in which CNTs are dispersed in rubber matrices as if they are cell membranes.[22] An environmentally resistant rubber seal (CNT/fluoroelastomer (FKM) composite) with a sealing ability of 260 °C and 239 MPa, which far exceeds the current sealing ability (175 °C and 140 MPa, standard specification), has already been developed.[22] Thanks to this development, the drilling rate of raw oil is expected to significantly improve, contributing to the stable supply of oil resources.

The expected application areas of CNTs range widely. The commercialization of the PAN-based CFs started from fishing rods and golf clubs; then in approximately 10 years,

it expanded to aerospace-related fields. Since then, the demand for carbon fibers (CFs) in common industries has also been increasing. CNTs appear to be heading in a similar direction of development, and scientific support for the development of CNTs from fundamental to application fields is hoped for in the future.

6. Carbon Fixation Technology and CNT Safety to be Successfully Accepted in the Society

One of the reasons for the high cost of synthesizing CNTs is the need for catalysts, however, Su *et al.* proposed the use of inexpensive natural minerals instead.[23] Our research group synthesized CNTs using garnet sand (approximately 150 yen/kg) as the catalyst and city gas as the carbon source. As a result, we found that this method enables the synthesis of MWCNTs with high efficiency.[24] The as-produced MWCNTs are easily separated from the garnet sand by sonication in the water. Furthermore, the garnet sand can be reused. We came to the conclusion that this method is worthy of consideration as an inexpensive synthesis method.

In CCVD method, the methane source is reacted with the metal catalyst such as iron, then CNTs are synthesized as the reaction product, and a mixed gas of hydrogen and unreacted methane is obtained as the by-product. This mixed gas is a new fuel, hythane; the carbon atoms in the methane are fixed in CNTs, contributing to the reduction of greenhouse gases. CNTs are synthesized from abundant methane, hydrogen fuel can be produced to realize a hydrogen economy, and the CNT synthesis process can serve as a carbon fixation process. Not only are some companies seeking a direction for CNT synthesis on the basis of this concept, but oil-producing countries are also interested in this method from the viewpoint of the future-oriented utilization of oil resources.

The development of CNT-related material technology should be based on the concept of "safety for success" or "safe innovation" and the abidance of the correct risk control, from the initial to the final processes of products, following the principle of "responsible production and application".[25–28] It is important to establish and share international evaluation criteria developed for the complete safety and toxicity evaluation of CNTs; moreover, I hope that the development of the applications of CNTs will be promoted further on the basis of such criteria. As Takagi *et al.*[29] reported, malignant mesothelioma induced in mice to which CNTs were intraperitoneally administered. Without question, we must pay special attention to all processes related to CNTs until a socially acceptable risk control system can be established. Through the practice of safe and responsible production, application, distribution, and disposal should be carried out under a life-cycle assessment for the commercialization of CNTs. I hope that a leading model to promote scientific and technological research and industrial promotion of CNTs will be established on the basis of the precautional approach or control banding, which all of academia should pay attention and expend effort to this end. To achieve this, the risks and benefits of CNTs should be correctly understood. At the same time, it is necessary for all stakeholders to participate in open discussion, and for the use of CNTs to be widely accepted by society through the disclosure of information, promoting to a safe and green innovation of using CNTs under social agreement beyond the scheme of science and technology. Steady progress in the safety evaluation of CNTs will lead to success of CNTs (safety for success).[25,30] I hope that CNT science and technology, expected to greatly contribute to green technology, can serve as a 21st-century model of material development.

7. Future Challenge

By using CCVD method, I am expecting improvements such as the precise control of chirality, the suitable and designed length control and synthesis efficiency of CNT. The advancement of applied basic science used to create innovative applications, performing biological safety evaluation that will encourage social acceptance of CNTs, and the development of safe-controlled CNT structures in the future are highly anticipated in the near future. Through these activities, CNTs will be sure to contribute to green innovation in the 21st century.

Carbon has played an important role at the turning points of cultural history, such as pencil lead, the electrical bulb filament made of carbonized bamboo developed by Edison, and CFs that have enabled humans to go into space beyond the earth. Carbon is an "old but new" material, and Professor H. W. Kroto predicted that the 21st century will be the carbon age; I hope these words will come true. Much expectation is concentrated particularly on nanocarbon, such as fullerene, CNTs, and graphene which are playing leading roles.

Information has been collected and accumulated in various fields, from fundamental science, application basics, safety and toxicity evaluation, and precautious approach, to risk control. Comprehensive development, including fundamental and applied science, safety evaluation, and the establishment of control methods, and the abidance of ethical issues will be increasingly important for realizing CNT green innovation under the concept of "safety for success" and "safe innovation" in the future. I hope that CNTs can meet the demands of society on a global basis by overcoming the four hurdles, namely, science, technology, economy, and social acceptance.

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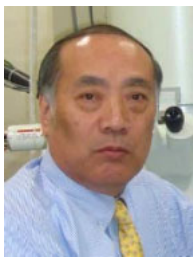

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