JAPANESE JOURNAL OF APPLIED PHYSICS Vol.45, No.6A (2006) pp.4883-4892[Part1] Invited Review Paper

Development and Application of Carbon Nanotubes

Morinobu Endo, Takuya Hayashi, Yoong Ahm Kim and Hiroyuki Muramatsu

In this review, we introduce the production methods and applications of carbon nanotubes. Carbon nanotubes are now attracting a broad range of scientists and industries due to their fascinating physical and chemical properties. Focusing on the chemical vapor deposition (CVD) method, we will briefly review the history and recent progress of the synthesis of carbon nanotubes for the large-scale production and double-walled carbon nanotube production. We will also describe effective purification methods that avoid structural damage, and discuss the electrochemical, composite, and medical applications of carbon nanotubes.

KEYWORDS:carbon nanotube, CVD, lithium ion batteries, electric double layer capacitors, nanocomposites

1. Introduction

After 30 years from their first synthesis by Endo in 1976¹⁾ and 15 years from their detailed structural characterization by lijima in 1991,²⁾ carbon nanotubes have grown from a material of dreams to a "real-world" material that has already found its application fields. The production capability for carbon nanotubes is growing every year in an exponential degree, and as a consequence the price is steeply descending. This is leading to even more use of carbon nanotubes in various fields, such as composites, energy devices, electronic applications, and medical applications, to list a few.

For novel applications of carbon nanotubes, the control of diameter, chirality, the number of layers and purity is crucial. However, at the moment, there is almost no control over these factors. Therefore, we need to address these issues to bring out the inherent potential of carbon nanotubes in full. In this article, we will provide an overview of the preparation of carbon nanotubes and nanofibers via catalytic chemical vapor deposition methods, which are used for controlling the diameter and number of layers of carbon nanotubes. Finally, we will explore the major applications of various types of carbon nanotubes.

2. Methods of Preparing Carbon Nanotube: Historical View

The initial catalytic chemical vapor deposition (CCVD) method for producing carbon nanotube developed by Endo was a so-called seeding method.¹⁾ In this method, the substrate, dispersed with small metal catalysts such as iron particles, was set into the hotspot of the furnace under a constant flow of hydrocarbon such as benzene and hydrogen and argon mixture gas (Fig. 1). The temperature of the furnace was around 1000°C, and the fibrous materials grew on the surface of the substrate from the iron particle.





Fig.2. Transmission electron microscope image of fibrous carbon grown by seeding method. An iron catalyst particle is observed at the tip of the inner tube.

Faculty of Engineering, Shinshu University and Institute for Carbon Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan (Received December 28, 2005; accepted March 10, 2006; published online June 8, 2006) ©2006 The Japan Society of Applied Physics







Fig.4. Illustration of floating method setup (left) and its growth model (right). The basic growth mechanism is the same as those of other CCVD methods, since the growth initiates from the catalyst.

The obtained fibrous carbon material had the carbon nanotube in the core, and deposited carbons on it (Fig. 2). The diameter of the fibrous carbon was several micrometers and the length was up to several centimeters. The metal catalyst particle was found in the core of the nanotube, proving that carbon nanotube growth started from the catalyst particle. Moreover, the catalyst particles were located at the tip of the tube. From these results, Endo proposed the tip-growth model of carbon nanotube. As shown in Fig. 3, carbon is supplied to the catalyst particle, and when the carbon is saturated, it starts to form the tubular carbon structure by using the spherical catalyst particle as a template. This growth lifts the catalyst particle upwards resulting in the image shown in the figure. We have to note that whatever the growth model is, be it tip growth or root growth, the catalyst particle

is the starting point of the growth of carbon nanotubes in the CCVD process.

Due to the strong demand for this carbon nanotube in the market, Endo had to develop a continuous growth process of carbon nanotube, since the seeding method described above was a non-continuous method, and was unsuitable for industry-scale production. After a while, Endo managed to develop the continuous method called the floating reactant method.³⁾ This method makes use of a vertical furnace, in which the metal catalyst, carbon source, and gases are fed from the top end of the furnace (Fig. 4). While the catalyst particles are floating, gradually falling inside the furnace, the tube growth and carbon deposition processes occur. This, at the bottom end of the furnace, results in the carbon nanotubes. This method was very effective for the

volume production of carbon nanotubes, and the quality of the product was high as well. This production system is now used in a Japanese company and their carbon nanotubes are widely available in the market.

In a catalytic CVD process, we cannot get rid of catalysts while producing carbon nanotubes. Therefore, depending on the application of the fibers, the catalysts must be removed after the synthesis. There are many ways to remove the catalysts, such as high-temperature heat treatment or acid washing.⁴⁻⁶⁾ Heat treatment was carried out in a high-temperature furnace at around 3000°C with an inert gas. It effectively evaporates the catalyst particles from the carbon nanotubes and almost no metal is detected after heat treatment. Acid washing is mostly performed in thinner tubes to remove the catalysts and the unreacted



Fig.5. Image showing growth of nanotubes from substrate such as zeolite. The pore restricts the aggregation of the catalytic particles, and efficiently produces single walled carbon nanotubes.

metal particles. HNO_3 and HCI are often used to remove the metal particles.

3. Controlling Growth

As the demand in the market grew, the need for various kinds of carbon nanotubes grew as well. There are so many parameters involved in the synthesis of carbon nanotubes; the size of the catalyst particle is just one of them, but is considered to be playing the major role in the CVD process along with the carbon source. As briefly mentioned before, the control over the diameter of the catalyst particle is the key factor in controlling the diameter and number of layers of the tube. If the diameter of the catalyst remains small, the diameter of the synthesized tubes generally becomes small accordingly. Therefore, if we can control catalyst particle size, we can nearly control the diameter of the tube. There are many ways to grow fibrous carbon, and the number of ways to control catalyst size is increasing, as the importance became broadly recognized among researchers.

A widely applied method is to use a substrate and place the catalyst particles on it. There are many variations depending on the choice of substrate and the way of controlling (or limiting) the size of the catalysts. One of the major substrates is the quartz substrate, 7-9) and metal particles are deposited either by dip coating or spraying a metal solution on the substrate. It is important to try to limit the aggregation of the catalyst particles, and keep catalyst size as homogeneous as possible. This is usually done by controlling the condensation of metals and by strictly controlling the temperature of the substrate. A dual-phase catalyst is sometimes used to inhibit the aggregation. By performing these, catalyst diameter usually remains in the range of 1-2nm, and can be made larger by the aggregation. However, for the purpose of obtaining the single walled carbon nanotube (SWCNT), it is desirable for catalyst size to remain small. The tubes on the substrate usually grow vertically from the substrate, and are easily peeled as nanotube mats, which make it easier to use them for optical polarizers and similar applications.

Another way is to use ceramic particles such as Al_2O_3 , MgO,¹⁰⁾ and zeolites (**Fig.** 5). These particles, whose size ranges from ~100nm to ~100 µm, are mixed with metal solution in order to prepare ceramic-supported catalysts. Using the particles has the advantage of gaining as much surface area as possible for supporting the catalyst, on which the nanotubes grow. To control catalyst size, again, metal concentration and the temperature of the furnace are important. By suitably controlling the diameter of the metal catalyst particles, we can even obtain a very small tube in a freestanding form.¹¹⁾ Since the tubes grow around the ceramic particles, some process for removing these particles is needed. It is also important to remove the catalyst particles, and it is convenient if we can perform the removal of catalysts and ceramic particles at the same time. Depending on the ceramic used to support the catalysts, the acid for removing the ceramics varies among HF, HCI, or HNO₃.

We have to note that the carbon source with carrier gas used in the synthesis also plays an important role for the ease of controlling the layer number of the tubes. Depending on the carbon source type, the activity of the catalyst particle can remain for a longer period, resulting in longer tubes. On the other hand, if the choice of carbon source is bad for the growth conditions selected (such as furnace temperature and flow rate), we end up with a mixture of single-, double-, and multi-walled nanotubes, along with deposited amorphous carbons. When the ease of carbon source decomposition is high, or the carbon flow rate is too high, it is very difficult to efficiently synthesize single- or double walled nanotubes, and the process mostly results in multi-walled carbon nanotubes or even lots of amorphous carbons. Therefore, we need to use the carbon source with low carbon content, which is rather difficult to decompose, such as ethanol/ethane and methanol/ methane, at the appropriate feed rate, for the efficient synthesis of single- and double-walled carbon nanotubes. This low-carbon-content carbon source simplifies the control of layer number.

Since the applications of multi-walled carbon nanotubes usually do not have a strict requirement for the controlled diameter, it is easier to synthesize the multi walled carbon nanotubes than single- or double-walled carbon nanotubes. As mentioned in the above section, CCVD is probably the only method suitable for the mass production of multi walled carbon nanotubes. As in the case of single- and double-walled carbon nanotube growth, catalyst particles can be located on



Fig.6. (a) SEM image of as-grown carbon nanotubes. (c) TEM image of as-grown carbon nanotubes. (b) SEM image of purified carbon nanotubes. (c) TEM image of as-grown carbon nanotubes. (c) TEM image of purified carbon nanotubes. It is clear from the images that the purification process effectively removes the catalyst support and unwanted carbons.

the substrate or float in the atmosphere. Since the CCVD uses the metal catalyst, the growth of the tube starts from the metal particle. Therefore, the particle size of the metal catalyst determines the size of the tubes. The growth mechanism is expected to be the same as that of the single- and double-walled nanotube case, except the case of multiple-layer growth.

The purification process is required to obtain the best part of the synthesized nanotubes. When we say carbon nanotubes, we imagine the perfect tubular structure. However, it is not what we always obtain when we synthesize the tubes via the CCVD (and other) process. Therefore, we need to somehow select the tubes that are as ideal as possible, from the obtained material. The purification process is usually a repetition of a two-step process. The first step is acid reflux, and the second step is annealing. Acid reflux is usually performed using HNO₃, H₂SO₄, or HCl, which washes the metal catalysts and impurity carbons. Annealing is performed in oxygen or in some inert gases to burn the defective tubes and carbon particles (Fig. 6). After repeating these steps several times, the purity of the tubes become high enough, so that it becomes difficult to find the trace of other carbon impurities by Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). We have to note that it does not mean that

they are perfect or homogeneous tubes. In the purification of double walled carbon nanotubes, annealing is used to burn single walled carbon nanotubes, which are more unstable than double-walled nanotubes, and therefore burn faster than the double-wall nanotubes.

4. Applications of Various Types of Carbon Nanotubes

Depending on the size and morphology of the fibrous carbons, the application varies a lot. When the diameter is large, they are used in energy devices such as fuel cells, lithium ion secondary batteries, and electric double-layer capacitors. Large fibers can also be used in composites as a filler material, for reinforcing



Fig.7. (a) SEM micrographs of anode sheet containing carbon nanofibers/nanotubes in commercial Li ion battery, and (b) cyclic efficiency of synthetic graphite, heattreated at 2900°C, as function of weight percent, in range 0 to 1.5V, with current density of 0.2mA/cm².

the composites, and as a thermal conductor. As the diameter of the fibrous carbon decreases, the applications also scale down in size. Smaller fibrous carbons can be used as a filler of three-phase composites, such as the resin/large carbon fiber/small carbon nanotube composite. In this composite, nanotubes fill and reinforce the resin that exists around the fiber. The nanotubes in the resin also act as an interconnection between the fibers to enhance the electrical and thermal conductivity of the composite. Nanotubes are used as field emitters and optical polarizers, as well. For the small carbon nanotubes, electronic devices, such as FETs, and interconnects are under development.

4.1 Electrochemical system

4.1.1 Lithium-ion battery

The outstanding mechanical properties and the high surface-to-volume ratio (due to their small diameter) make carbon nanotubes potentially useful as an anode material¹²⁻¹⁷⁾ or as an additive¹⁸⁾ in lithium-ion battery systems. An SEM image of an electrode containing 10wt% carbon nanotubes as the additive shows a homogeneous distribution of nanotubes in synthetic graphite [Fig. 7(a)]. Figure 7(b) reveals the cyclic efficiency of a synthetic graphite anode as a function of the weight percent of multi-walled carbon nanotubes (MWNTs). With increasing weight percent of carbon nanotubes, the cyclic efficiency of the synthetic graphite battery anode increases continuously, and in particular, when 10wt% nanofibers/nanotubes were added, the cyclic efficiency was maintained at almost 100% up to 50 cycles. At higher concentrations, the nanotubes interconnect graphite powder particles together to form a continuous conductive network. The characteristics of carbon nanotubes when used as a filler in the electrodes of Li-ion batteries can be summarized as follows; (a) the small diameter of the nanofibers makes it possible to distribute the fibers homogeneously in the thin electrode material and to introduce a larger surface area to react with the electrolyte; (b) the improved electrical conductivity of the electrode is related to the high electrical conductivity of the tubes, and the network formation of the nanofibers/ nanotubes with the graphite particles in the anode can be obtained to form a tube mat; (c) the relatively high intercalation ability of nanotubes does not lower the capacity of anode materials itself upon cycling; (d) a high flexibility of the electrode is also achieved due to the network formation of the nanotube in a tube-mat structure; (e) the high endurance of the electrode is realized because nanotubes absorb the stress caused by the intercalation of Li ions; (f) improved penetration of the electrolyte is attained due to the homogeneous distribution of the tubes surrounding the anode material, and (g) the cyclic efficiency of Li-ion batteries is improved for a relatively long cycle when compared with carbon black.

4.1.2 Additives to electrodes of lead-acid batteries

In order to increase the conductivity of electrodes in lead-acid batteries, carbon nanotubes of different weight percents are added to the active anode material (average diameter = $2-5\mu$ m) of the positive electrode. The resistivity of the electrode is lowered for the case of 1.5 wt% nanotube addition. When this sample (0.5-1 wt%) is incorporated in the negative electrode, the cycle characteristics are greatly improved as compared with that of an electrode without additive (Fig. 8).¹⁸⁾ This is probably due to the ability of carbon nanotubes to act as a physical binder, resulting in electrodes which undergo less mechanical disintegration and shedding of their active material than electrodes without carbon nanotubes. Therefore, it is expected that the use of carbon nanotubes as an electrode filler should lead to improved cyclic behaviors for the electrodes in lead-acid batteries as compared with those using conventional graphite powder, because the unusual morphology of carbon nanotubes, such as the concentric orientation of their graphite crystallites along the fiber cross section, induces a high resistance to oxidation, and furthermore the network formation would induce an improved utilization of the active material in the electrode.

4.1.3 Electric double-layer capacitor

The advantage of the electric doublelayer capacitor (EDLC) is considered to be its high discharge rate,¹⁹⁾ thus making it applicable as a hybrid energy source for electric vehicles and portable electric devices.²⁰⁾ EDLC containing carbon nanotubes in the electrode exhibited relatively high capacitances resulting from the high surface area accessible to the electrolyte.^{17,21,22)} On the other hand, the most important factor in commercial EDLC is considered to be the overall resistance on the cell system. In this context, carbon nanotubes and nanofibers with enhaced electrical and mechanical properties can be applied as an electrical conductive additive in the electrode of EDLC. It has been demonstrated that the addition of carbon nanotubes results in an enhanced capacity at higher current densities, when compared with electrodes containing carbon blacks.23)

4.1.4 Fuel cell

Fuel cells have been considered as nextgeneration energy devices because such systems transform the chemical reaction energy from hydrogen and oxygen into electric energy.²⁴⁾ Carbon nanotubes decorated with metal nanoparticles as an electrode has doubled the fuel cell performance due to the increased catalytic activity of nanotubebased electrodes.²⁵⁻²⁷⁾ In this context, we have reported the efficient impregnation of Pt nanoparticles (outer diameter < 3nm) on cup-stacked-type carbon nanotubes.²⁸⁾ The method involves the dispersion of the fibers in H₂PtCl₆, followed by low-temperature



Fig.8. Effects of carbon nanotubes embedded in conductive filler in polyvinylidene-derived carbon electrode, compared with those of carbon black/polyvinylidene composite.



Fig.9. HRTEM image of highly dispersed Pt nanoparticles deposited on both outer and inner surfaces of shortened stacked-cone nanotubes/nanotubes.

annealing. Pt particle deposition is always homogenous, and can be controlled selectively on the outer or inner core using the hydrophobic nature of the material (see Fig. 9). Since the level of Pt particle activity on the fibers is high, this material could find applications as efficient catalysts and in biological devices. It is anticipated that carbon nanotube technology will contribute to the development of fuel cells, as a catalyst support, and also as a main component as bipolar systems. However, additional basic and applied research is necessary.

4.2 Multifunctional fillers in polymer composite

It has been shown that carbon nanotubes could behave as the ultimate one-dimensional material with remarkable mechanical properties.^{29,30)} The density-based modulus and strength of highly crystalline SWNTs are 19 and 56 times that of steel. On the basis of a continuum shell model, the armchair tube exhibits a larger stress-strain response than the zigzag tube under tensile loading [Fig. 10(a)]. Also highly improved mechanical properties are expected owing to the strong carbon-carbon covalent bond depending strongly upon the atomic structure of nanotubes and the number of shells [see Figs. 10(b) and 10(c)]. Moreover, carbon nanotubes exhibit enhanced electrical and thermal conducting properties; better than those of copper. Therefore, carbon nanotubes (singleand multi-walled) have been studied intensively as fillers in various matrices, especially polymers.³¹⁻³⁵⁾ The best utilization of the intrinsic properties of these fibrous nanocarbons in polymers could be achieved by optimizing the interface interaction of the nanotube surface and the polymer. Therefore, surface treatments via oxidation in conjunction with the polymer or epoxy could be used in order to improve adhesion properties between the filler and the matrix. This results in a good stress transfer from the polymer to the nanotube. There are various surface oxidative processes, such as electrochemical, chemical and plasma techniques. From the industrial point of view, ozone treatment is a very attractive technique. In addition, the dispersion of



Fig.10. (a) Stress-strain response of CNT under tensile loading, (b) HRTEM image of bent double wall carbon nanotube and (c) HRTEM image of twisted single wall carbon nanotube.

nanotubes/nanofibers in the polymer should be uniform within the matrix.

The smallest working composite gear has been prepared by mixing nanotubes into molten nylon and then injecting into a tiny mold. As shown in Fig. 11, the diameter of this gear is as small as that of human hair. This piece exhibits high mechanical strength, high abrasion resistance and also good electrical and thermal conductivity.

When cup-stacked-type carbon nanotubes are incorporated in polypropylene, the improvement in tensile strength with increasing the amount of nanotubes is really remarkable (up to 40%). This remarkable result can be explained by the particular morphology of cup-stacked-type carbon nanotubes. In other words, a large portion of edge sites on the outer surface of nanotubes might act as nucleation sites and then higher crystallization of polypropylene, resulting in good adhesion between nanotubes and polymers (good stress transfer), is achieved. Recently, various studies on the nucleation effect of nanotubes on the crystallization of semi crystalline polymer have been reported.36-38)

4.3 Medical applications

The high-purity multi-walled carbon nanotubes with diameters ranging from 40 to 90 nm (aver. = 80 nm) used in this study were produced on a large scale through a right combination of a catalytic chemical vapor deposition synthetic method^{1,3)} and subsequent heat treatment at 2800°C for 30 min in argon atmosphere. These tubes are relatively linear and have a long tubular morphology.¹⁸⁾ In addition, these tubes are highly crystalline [see TEM image in Fig. 12(a)] and contain an extremely small portion of iron (below 100ppm). It is noteworthy that metal iron, which is the essential component for nanotube growth, has to be removed completely because very recently published research revealed that metallic compounds incorporated in carbon nanotubes generate toxicity.^{39,40)} Thus, thermal annealing could be the best choice both for removing the remaining metal compounds in carbon nanotubes and for improving structural integrity.



Fig.11. SEM image of smallest working gear (carbon nanotube/nylon composite); the inset shows the fractured surface.



Fig.12. (a) High-resolution TEM image of carbon nanotubes (note that linear graphene layers are highly developed along the tube length), (b) photographs of transparent nylonderived and opaque black-colored nanotubefilled nanocomposite-derived microcatheters, SEM images of cross section (c) at low resolution and (d) high resolution. It is noteworthy that carbon nanotubes were dispersed homogeneously in nylon polymer.



Fig.13. Cross-sectional views of pure nylon-derived microcatheter (a) and nanotube-filled nanocomposites-derived microcatheter (b) inserted into the arteries.



Fig.14. SEM images of extraluminal surface of pure nylon-derived microcatheter (a) and nanotube-filled nanocomposites-derived microcatheter (b).

Nylon-12 and 10wt% carbon nanotubes were mixed using a conventional mixer, and then the obtained dry mixture was fed into a conventional twin-screw extruder in order to fabricate a microcatheter (inner diameter = 0.46 mm, outer diameter = 0.53 mm) [see Figs. 12(b) and 12(c)]. The nanotube-filled nanocomposite-derived microcatheter has opaque black color while the pure nylon-derived catheter is highly transparent. The relatively homogeneous distribution of carbon nanotubes in nylon polymer was confirmed by observing the fractured surface of the nanotube-filled microcatheter [see SEM image in Fig. 12(d)].

4.3.1 Anti-thrombogenicity and low blood coagulation of nanotube-filled nanocomposites-derived microcatheter

We utilized adult beagle dogs (9–11kg) for thrombus formation *in vivo*. The bilateral femoral and common carotid arteries, with the length of approximately 5cm, were exposed surgically. These arteries were taped to avoid bleeding during the replacement of the nano-tube-filled microcatheter to be tested, which was inserted into the artery at an angle of approximately 45° from proximal to distal sites. A detailed experimental procedure was published in our previous study.⁴¹⁾

We observed cross sections of the removed artery, which was stained by hematoxyline and eosin. The pure nylon-derived microcatheter [Fig. 13(a)] exhibited a marked formation of a thrombus with a dark violet color in the intra-arterial space. On the other hand, the nanotube-filled nanocomposite derived microcatheter [Fig. 13(b)] exhibited highly reduced thrombus formation. From this result, it is sure that the nanotube-filled microcatheter has lower reactivity toward blood than the pure nylon-derived one, if the blood stream is not disturbed. Even though both microcatheters exhibit a fibril-like network and blood cells as shown in Fig. 14, the nanotubefilled microcatheter shows smaller amount of fibrils and blood cells [Fig. 14(b)]. As a result, it is confirmed that the nanotube-filled nanocomposites-derived microcatheter exhibits anti-thrombogenicity and low blood coagulation.

4.3.2 Biocompatibility of nanotube-filled nanocomposites-derived microcatheter

We observed very similar levels of CD4⁺ T-cell concentration for pure nylon- (51.5 \pm 2.7%) and nanotube-filled nanocompositederived (49.7 \pm 2.0%) microcatheters after one week of postimplantation [see Fig. 15(a)]. Also, CD8⁺ T-cell concentrations for both microcatheters were 14.3 \pm 0.8 and 16.3 \pm 0.9%, respectively [Fig. 15(b)]. As a result, a low CD4⁺/CD8⁺ T-cell ratio (3.07 \pm 0.1) for the nanotube-derived microcatheter was observed as compared with that for the pure nylon-derived microcatheter (3.72 \pm 0.25). A major histocompatibility complex (MHC) class I pathway of the antigen-antibody response system was developed in case of the nylon-derived microcatheter. From macroscopic appearances of an implanted tissue (Fig. 16), we observed the embedded pieces of the





Fig.16. Macroscopic aspect of skin tissue implanted microcatheter; (a) nylon-derived, (b) nanotube-filled nanocomposite-derived microcatheters.



Fig.17. Light microscopic images of skin tissue implanted (a) nylon-derived microcatheter and (b) nanotube-filled microcatheters at different resolutions.

nylon-derived microcatheter encapsulated by an inflammatory thick membrane with new vessels characteristically, but not in the case of the nanotube-filled microcatheter. From histopathological aspects of the implanted microcatheters after 1 week (Fig. 17), granulomatous tissue with cellular infiltration remarkably appeared in the nylon-derived microcatheter [Fig. 17(a)]. In addition, the granuloma formation encapsulating a mass of the nylon-derived microcatheter was quite compact as compared with that in the case of the nanotube-based microcatheter [Fig. 17(b)].

5. Conclusions

In this paper, we have reviewed the possible routes to the large-scale synthesis of carbon nanotubes (single- and multi-walled), with an emphasis on their applications in electrochemical systems and polymer nanocomposites. The unique electronic properties of nanotubes make them also good candidate materials in the electronic industry, so that silicon-based technologies could be replaced or supplemented by nanocarbons. The possible applications of carbon nanotubes range from electronics, field-emission displays, energy storage devices, functional fillers in composites, and biomedical applications. These have attracted both industrial and academic interest. However, due to the gap between basic research and the requirements of real-world applications, small nanotubes are facing technical difficulties such as dispersion, chirality selection, and handling. Therefore, it is important to smoothly and efficiently transfer the basic findings to industries to commercialize the novel technologies rapidly.

- A. Oberlin, M. Endo and T. Koyama: J. Cryst. Growth **32** (1976) 335.
- 2) S. lijima: Nature **354** (1991) 56.
- 3) M. Endo: CHEMTECH 18 (1988) 568.
- 4) T. W. Ebbesen, P. M. Ajayan, H. Hiura and K. Tanigak: Nature **367** (1994) 519.
- K. B. Shelimov, R. O. Esenaliev, A. G. Rinzler, C. B. Huffman and R. E. Smalley: Chem. Phys. Lett. 282 (1998) 429.
- 6) J. M. Moon, K. H. An, Y. H. Lee, Y. S. Park, D. J. Bae and G. S. Park: J. Phys. Chem. B **105** (2001) 5677.
- S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi and M. Kohno: Chem. Phys. Lett. **360** (2002) 229.
- Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo and S. Maruyama: Chem. Phys. Lett. **385** (2004) 298.
- K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura and S. lijima: Science **306** (2004) 1362.
- M. Endo, H. Muramatsu, T. Hayashi, Y. A. Kim, M. Terrones and M. S. Dresselhaus: Nature 433 (2005) 476.
- T. Hayashi, Y. A. Kim, T. Matoba, M. Esaka, K. Nishimura, T. Tsukada, M. Endo and M. S. Dresselhaus: Nano Lett. **3** (2003) 887.
- M. Endo, J. Nakamura, Y. Sasabe, T. Takahashi and M. Inagaki: Trans. IEE Jpn. A **115** (1995) 349.
- K. Tatsumi, K. Zaghib, H. Abe, S. Higuchi, T. Ohsaki and Y. Sawada: J. Power Source 54 (1999) 425.

- 14) E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy and F. Beguin: Carbon **37** (1999) 61.
- G. T. Wu, C. S. Wang, X. B. Zhang, H. S. Yang, Z. F. Qi, P. M. He and W. Z. Li: J. Electrochem. Soc. **146** (1999) 1696.
- B. Gao, A. Kelinhammes, X. P. Tang, C. Bower, Y. Wu and O. Zhou: Chem. Phys. Lett. **307** (1999) 153.
- 17) E. Frackowiak and F. Beguin: Carbon **40** (2002) 1775.
- M. Endo, Y. A. Kim, T. Hayashi, K. Nishimura, T. Matushita, K. Miyashita and M. S. Dresselhaus: Carbon **39** (2001) 1287.
- B. E. Conway: Electrochemical Supercapacitors-Scientific Fundamentals and Technological Applications (Kluwer Academic, Dordrecht, 1999).
- 20) K. Miyadera: Toyota Tech. Rev. **52** (2002) 22.
- C. Niu, E. K. Sickel, R. Hoch, D. Moy and
 H. Tennent: Appl. Phys. Lett. **70** (1997) 1480.
- 22) K. H. An, W. S. Kim, Y. S. Park, J. M. Moon, S. C. Lim, Y. S. Lee and Y. H. Lee: Adv. Mater. **11** (2001) 387.
- T. Takeda, R. Takahashi, Y. J. Kim, K. Koshiba, K. Ishii, T. Kasahi and M. Endo: Tanso **196** (2001) 14 [in Japanese].
- 24) M. C. Williams: Fuel Cells 2 (2001) 87.
- 25) P. J. Britto, K. S. V. Santhanam, A. Rubio, A. Alonso and P. M. Ajayan: Adv. Mater. **11** (1999) 154.
- 26) G. Che, B. B. Lakshmi, E. R. Fisher and C. R. Martin: Nature **393** (1999) 346.
- T. Yoshitake, Y. Shimakawa, S. Kuroshima, H. Kimura, T. Ichihashi, Y. Kubo, D. Kasuya,

K. Takahashi, F. Kohai, M. Yudasaka and S. Iijima: Physica B **323** (2002) 124.

- 28) M. Endo, Y. A. Kim, M. Ezaka, K. Osada, T. Yanagisawa, T. Hayashi, M. Terrones and M. S. Dresselhaus: Nano Lett. **3** (2003) 723.
- 29) J. P. Lu: J. Phys. Chem. Solids 58 (1997) 1649.
- F. Li, B. S. Cheng, G. Su and M. S. Dresselhaus: Appl. Phys. Lett. **77** (2000) 3161.
- P. M. Ajayan, O. Stephan, C. Colliex and D. Trauth: Science 265 (1994) 1212.
- K. T. Lau and D. Hui: Composites, Part B 33 (2002) 263.
- 33) P. Calvert: Nature **399** (1999) 210.
- 34) A. A. Mamedov, N. A. Kotov, M. Prato, D. M. Guldi, J. P. Wicksted and A. Hirsch: Nat. Mater. 1 (2002) 190.
- 35) G. D. Zhan, J. D. Kuntz, J. Wan and A. K. Mukherjee: Nat. Mater. 2 (2003) 38.
- L. Valentini, J. Biagiotti, J. M. Kenny and
 S. Santucci: J. Appl. Polym. Sci. 87 (2003) 708.
- A. R. Bhattacharyya, T. V. Sreekumar, T. Liu, S. Kumar, L. M. Ericson, R. H. Hauge and R. E. Smalley: Polymer 44 (2003) 2373.
- 38) M. Cadek, J. N. Coleman, V. Barron, K. Hedicke and W. J. Blau: Appl. Phys. Lett. 81 (2003) 5123.
- F. Tao, B. Gonzalea-Flecha and L. Kobzik: Free Radical Biol. Med. 35 (2003) 327.
- M. Tsien, D. Morris, J. Pietruska, K. Jian, A. Kane and R. Hurt: Ext. Abstr. Carbon Conf. 2005, Kyeongju, Korea, 2005.
- 41) M. Endo, S. Koyama, Y. Matsuda, T. Hayashi and Y. A. Kim: Nano Lett. **5** (2005) 101.



Morinobu Endo studied electrical engineering and received his B.E and M.E degree from Shinshu University in 1969 and 1971, respectively, and obtained "Docteur d'Universite" in 1975 from the University of Orleans, France, then Ph. D. from Nagoya University in 1978. In his Ph. D. works, he developed the structural, synthetic research as well as physical properties analysis, mainly on multi-walled carbon nanotubes. He showed that they had a tubular structure of graphite layers grown by ultra-fine

iron particle by catalytic process, and developed to mass production process. This catalytic CVD process has been used as an industrially available mass production method, both substrate and floating catalyst processes. Present CCVD process has been expecting to grow the wide range of carbon nanotubes by controlling the growth site as well as their nanostructure.

Since 1990 he is a professor of the Department of Electrical and Electronic Engineering, Shinshu University. He has been awarded Carbon Society of Japan Award (1995). For his pioneering work and applications of carbon nanotubes, he received the Charles E. Pettinos Award from the American Carbon Society in 2001, Ishikawa Award (Ishikawa Carbon Science/Technology Promotion Foundation, 2003), Medal of Achievement in Carbon Science and Technology, American Carbon Society (*for the discovery of, and early synthesis work on, carbon nanotubes*, 2004).

His main research interests are science and applications of "nanocarbons" such as carbon nanotubes, and he has contributed to development of new composites and high-performance energy storage devices such as lithium ion battery, electric double layer capacitor, and fuel cell, based on such structure controlled advanced carbons.











Hiroyuki Muramatsu studied Electronic Engineering and received his B.E. from Gunma University in 2002. In 2004, he received his M.E. from Shinshu University. Now, he is a Ph. D. student at Shinshu University. His current research interests are the CVD synthesis and analysis of carbon nanotubes.