

УДК 54.057, 54.07, 539.25

Carbon Nanotube: Story in Ando Laboratory

Yoshinori Ando*

Department of Materials Science and Engineering,
Meijo University, Shiogamaguchi 1-501, Tenpaku-ku, Nagoya 468-8502,
Japan

Received 10.01.2010, received in revised form 30.01.2010, accepted 20.02.2010

Carbon nanotubes (CNTs) were serendipitously discovered as a byproduct of fullerenes by direct current (DC) arc discharge; and today this is the most-wanted material in the nanotechnology research. In this brief review, I begin with the history of the discovery of CNTs and focus on CNTs produced by arc discharge in hydrogen atmosphere, which is little explored outside my laboratory. DC arc discharge evaporation of pure graphite rod in pure hydrogen gas results in multi-walled carbon nanotubes (MWCNTs) of high crystallinity in the cathode deposit. As-grown MWCNTs have very narrow inner diameter. Raman spectra of these MWCNTs show high-intensity G-band, unusual high-frequency radial breathing mode at 570 cm^{-1} , and a new characteristic peak near 1850 cm^{-1} . Exciting carbon nanowires (CNWs), consisting of a linear carbon-chain in the center of MWCNTs are also produced. Arc evaporation of graphite rod containing metal catalysts results in single-wall carbon nanotubes (SWCNTs) in the whole chamber like macroscopic webs. Two kinds of arc method have been developed to produce SWCNTs: Arc plasma jet (APJ) and Ferrum-Hydrogen (FH) arc methods. Some new purification methods for as-produced SWCNTs are reviewed. Finally, double-walled carbon nanotubes (DWCNTs) are also described.

Keywords: carbon nanotubes, synthesis methods.

In 1985 a new allotrope of carbon: fullerene was discovered by Kroto et al.[1] Subsequently, carbon nanotube (CNT) was discovered by Iijima [2] in 1991. Two years later, in 1993, CNTs consisting of a single graphene layer were reported by two groups: NEC [3] and IBM [4]. After that CNTs were classified into two kinds: single-wall carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Under this nomenclature, the first CNTs discovered in 1991 (containing two, five and seven coaxial cylinders) were MWCNTs. In this review, the term CNT is commonly used for both kinds of nanotubes, whereas SWCNT and MWCNT are specifically used where it is necessary to distinguish them. Although many books [5–9] and reviews [1–14] have been published on CNTs, the history of CNT discovery and production of CNTs in hydrogen arc discharge have not yet been described in sufficient detail. This reminds me to write the untold story of CNT discovery and unexplained science of hydrogen-arc discharge. CNTs are mainly produced by three methods: arc discharge method [2,15], laser ablation method [16], and chemical vapor deposition (CVD) method [17]. However, this review is confined to arc discharge method only.

1. Discovery of CNTs

In early 1980s, I used to grow ultrafine particles of SiC by direct current (DC) arc discharge between graphite cathode and a silicon anode (supported on another graphite rod) a short

*yando@ccmfs.meijo-u.ac.jp

distance apart [18]. In 1990, Krätschmer et al. reported mass production of fullerene [19, 20] by alternating current (AC) arc discharge between two graphite electrodes in contact. Then, I just removed the silicon block in my arc instrument and carried out DC arc discharge between two graphite electrodes 1–2 mm apart, and got a large volume of carbon soot including fullerene. Moreover, in my separated electrode method, I happened to get an additional carbon deposit at the end of the negative graphite rod, which did not occur in Krätschmer's AC contact-electrode method. I gave such a cathode deposit to my friend Sumio Iijima who serendipitously discovered exciting CNTs in that cathode deposit [2]. In the first paper of CNTs appeared in Nature [2] and in the second paper [21], the name "nanotubes" was not given but "microtubule" was used. From the third paper [22, 23], the name of CNTs was used by Iijima. As Iijima clearly wrote in the acknowledgement of the first paper (I thank Y. Ando for carbon specimens) [2], those CNT specimens were made by me. This fact is also written by Ebbesen in his review on CNTs [10]. Therefore, it is said that "Meijo University is the birth place of CNTs, and Ando is the first farmer of CNTs". I am aware tubular carbon structures were reported by Endo [24] well before Iijima's report [2]. Other reports [25–27] on carbon filaments also appeared before them [2, 24]. However, in true sense, nanometer-order diameter and coaxial seamless cylinders of graphite with helical arrangement of carbon atoms was first observed, understood and explained by Iijima [2]. Hence there should be no doubt that the credit of CNT discovery actually goes to Iijima alone. The story of those historical carbon specimens [2, 15] begins from early 1991. I heard the Krätschmer's work of mass production of fullerene [19, 20] from my friend Y. Saito (then in Mie University, now in Nagoya University) at Uyeda Symposium in early January 1991. Precise story of Krätschmer's work is written in Shinohara's book [28]. It was based on the conventional vacuum evaporation of graphite to make carbon film on microgrid to be used as transmission electron microscopy (TEM) specimen support [28]. One sharpened graphite rod was set against a flat graphite rod, and AC current was flown to evaporate the sharpened graphite rod by resistive heating. Krätschmer et al. [19] used inert gas into the chamber for mass production of fullerenes [1] like gas-evaporation method [29, 30].

From Saito's talk, I was motivated to try this mass production of fullerenes in my apparatus (Fig. 1) which I used to make ultrafine particles of SiC (together with Ohkohchi) [18]. The evaporation source of our mass production apparatus was DC arc discharge, and higher current (>100 A, as for industrial welding) was possible to apply. I replaced the Si block with a graphite rod [13, 15, 31] (Fig. 2), and put the two graphite electrodes a few mm apart. I successfully achieved mass production of fullerenes [32] by the end of January 1991. After the evacuation of the chamber, rare inert gas (He or Ar) of 100torr was introduced. Upon application of DC arc voltage of about 30V, the anode got evaporated and resulted in carbon ultrafine particles. This was just like a gas-evaporation method to make carbon ultrafine particles [33], and we used these carbon ultrafine particles as a sintering agent with boron for SiC ultrafine particles sintering [30]. As-grown carbon ultrafine particles were found to contain fullerenes up to 10 wt% [32]. By such an evaporation of graphite electrodes, we made a lot of fullerenes and measured their physical properties [34–36]. Moreover, metallo-fullerenes were also produced by using carbon electrode with rare earth metals (Sc, Y, and La) [37, 38].

In April 1991, Iijima (then at NEC, now at Meijo University) came to my laboratory (as he often used to do), watched my arc discharge apparatus carefully and praised my technique. "Yes, fullerene is new and exciting, but nowadays every third person is jumping in the fullerene camp. So personally I don't intend to carry fullerene research", he commented. I discussed with him the difference between Krätschmer's method and mine, and then he wanted to observe the

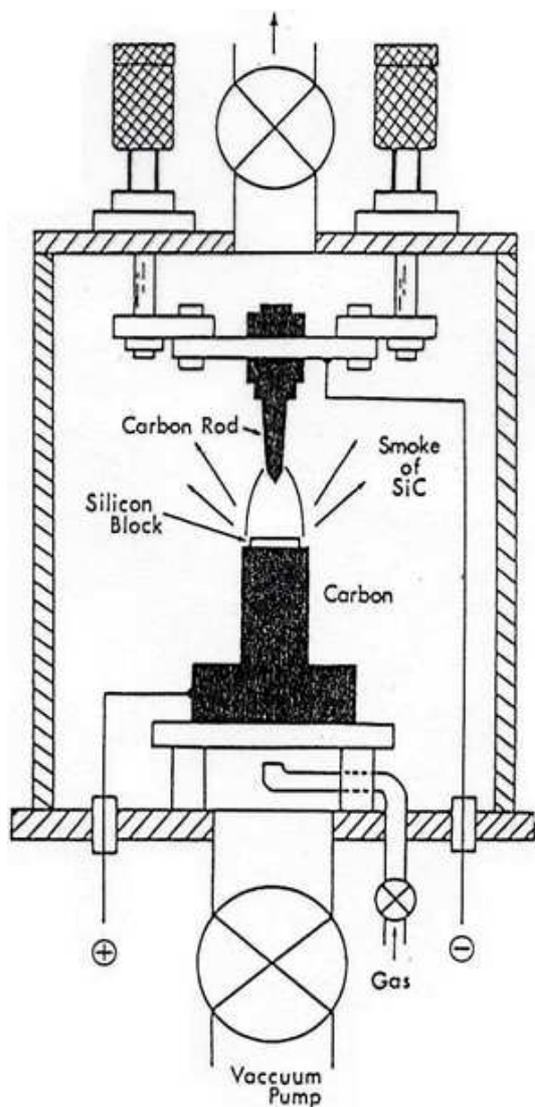


Fig. 1. Apparatus to make SiC smoke [18]

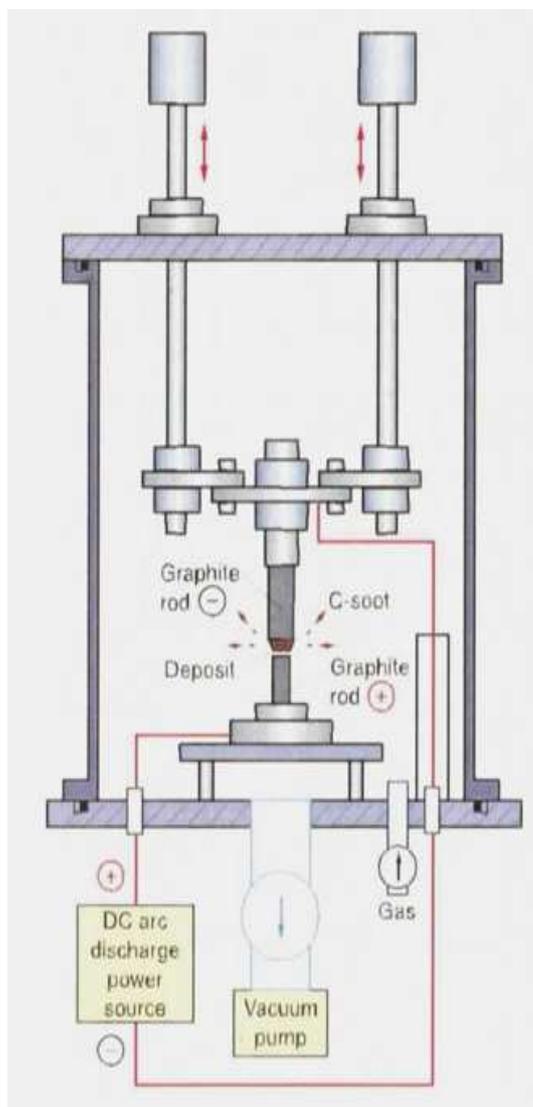


Fig. 2. Apparatus to make MWCNTs [13]

end-deposit of my graphite cathodes on his high resolution TEM (HRTEM). I gladly gave them to him, as I didn't have HRTEM in my University. Iijima possessed a deep interest in carbon [39], since 1980 and had already observed direct images of fullerenes by HRTEM [40]. Two months later he came back, and asked me to make more cathode deposits because they seemed to contain tubular carbon structures. I made similar cathode deposits under different ambient gases and handed over to him. One month later, he sent me a manuscript for *Nature* based on the observations from the first batch of my specimens. In that manuscript, I pointed out that the wall numbers (1, 2, 3) assigned in the circular and planar sections in Fig. 2 were inconsistent, but it was not corrected [2]. My name was acknowledged for providing the specimens. However, in the next paper in *Nature* [21] (based on the observations from my second batch of specimens) my name was given as a co-author. After that, we had several joint publications and that cooperation

is still going on.

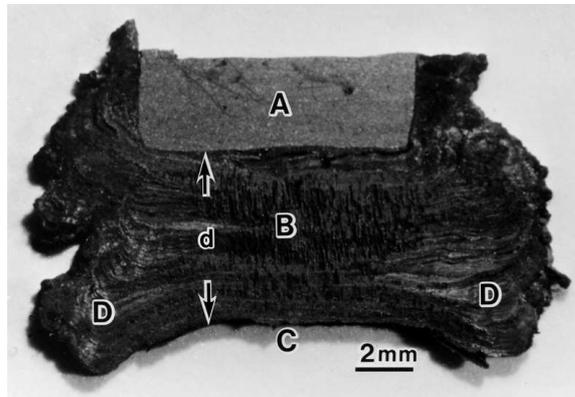


Fig. 3. Photo of cathode deposit [15]

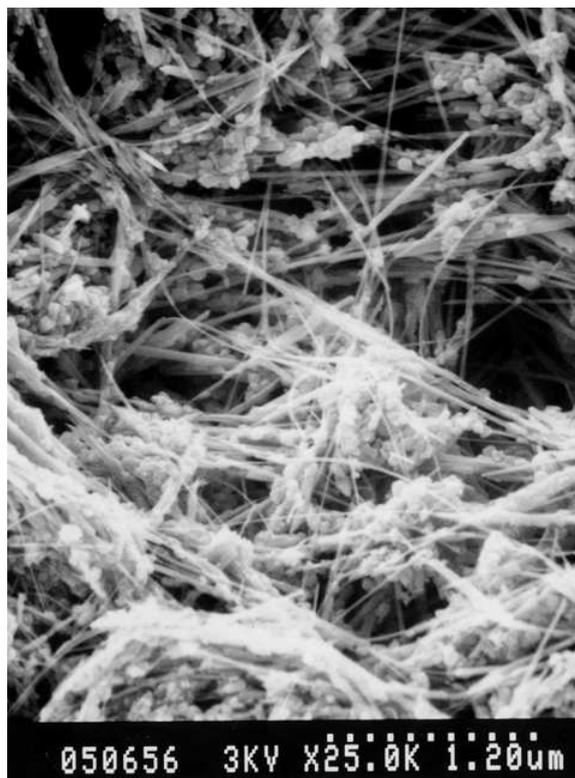


Fig. 4. SEM of MWCNTs [11]

In Fig. 3, an optical photograph of a section of cathode deposit cut by diamond saw is shown [15]. After several minutes of arc evaporation, a cathode deposit of several millimeters thick d is obtained. A in Fig. 3 is the tip part of the cathode, and B, C and D are the cathode deposit. Once, CNTs have been observed by HRTEM [2], we can easily confirm such fibriform CNTs by scanning electron microscope (SEM) also [15]. Fig. 4 is an example of SEM micrograph [11]

taken at the region B (Fig. 3), and we can see not only many CNTs but also co-existing carbon nanoparticles. Such fibriform CNTs could be observed by SEM at the surface C (Fig. 3) of the cathode deposit also [41]. However, in the both side regions D, only very few CNTs could be observed.

2. MWCNTs Produced by Various Conditions of Arc Discharge

All of CNTs produced by DC arc discharge using pure graphite electrodes in the cathode deposit were MWCNTs [41–45]. When DC arc current is applied to two pure graphite electrodes 1–2 mm apart, electrons emitted from the cathode hit the anode at high velocity, so the anode temperature gets higher than the cathode temperature and carbon atoms of anode evaporate. So the evaporated carbon atoms coagulate to carbon nanoparticles including fullerenes in the chamber. And a part (20–40%) of evaporated carbon gets deposited on the adjacent cathode (relatively at low temperature) and MWCNTs grow there.

However, when the anode graphite rod contains rare earth metals (which are effective to generate metallo-fullerenes [37, 38]) very high yield of MWCNTs is obtained in the cathode deposit [46, 47]. It seems that molten rare earth metal in the high-temperature arc works as a catalyst to increase the yield of MWCNTs in the cathode deposit. This is partly similar to the case of SWCNTs described later [48], though the place of SWCNT formation is entirely different. MWCNTs grow on the cathode only, while SWCNTs grow in the whole chamber space. As ambience, not only inert gases (He, Ar) but also CH₄ gas was used. The reason of using CH₄ was that it was found useful in getting good stoichiometry of SiC ultrafine particles in my earlier experiments [18]. So, I just wanted to see its effect in the CNT experiment. The result was that produced carbon species didn't contain fullerenes [49]. MWCNTs are more remarkable than the cases of inert gases [43–45], and co-existing carbon nanoparticles are not so many than the case of inert gases. To know the effect of arc on this non-inert gas, the chamber gas after arc-discharge was subjected to mass-spectroscopy. The results indicated that CH₄ gas was thermally decomposed to C₂H₂ and H₂, as shown by the chemical reaction formula:



In this reaction, the starting molar number is 2, while post-reaction molar number is 1+3=4. To confirm this point the chamber pressure was monitored during the arc discharge in CH₄ gas. It was noted that the chamber pressure at the end of arc discharge became just double of that before discharge. Incidentally, in the case of inert gas, there is a trivial increase in the chamber pressure after arc discharge (about 1.05 times) [45], which can be explained by temperature rise of ambient gas. This CH₄ gas reaction prompted me to check the arc evaporation in C₂H₂ and H₂ separately. The arc evaporation in C₂H₂ gas was similar to the case of CH₄, but the case of H₂ gas was quite different as described in the following section. The use of H₂ ambient gas for the production of MWCNTs was first done by Wang et al. (Northwestern University) [50], however their results were not so characteristic.

3. MWCNTs Produced by Hydrogen Arc Discharge

Arc discharge of graphite electrodes in hydrogen atmosphere is different from usual helium atmosphere in so many ways. For instance, cathode deposit [51] shown in Fig. 5 is classified to three regions, A, B and C. In region A, MWCNTs were observed as shown in Fig. 6(a) [52]. Carbon nanoparticles also co-exist, but their quantity is very little as compared with the case of inert gases (as seen in Fig. 4). Probably, hydrogen reacts with carbon species (not taking part in CNT growth) to make hydrocarbon. Because the coexisting carbon nanoparticles are very little, purification of them just by heating at 773 K in air for 30 minutes is easily down as seen in Fig. 6(b) [52]. A large number of thin and long MWCNTs and their bundles are observed in the SEM micrograph (Fig. 6(b)).

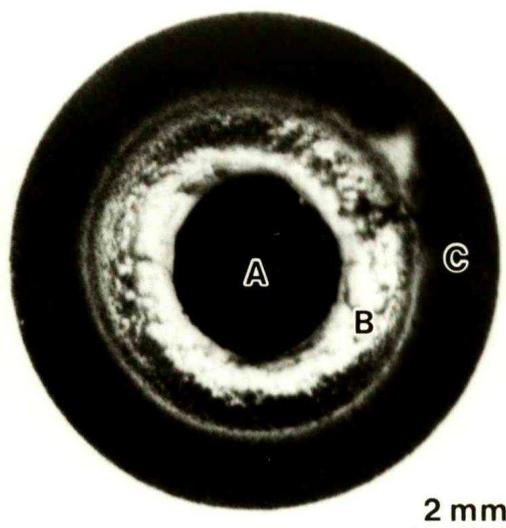


Fig. 5. Cathode deposit [51]

In the outer region C in Fig. 5, there are graphitic objects of quite different morphology [53], as shown in Fig. 7. Interlaced petal-like sheets form sponge of ellipsoid, and each sheet consists of several layers of graphene. We called it carbon nano-rose with graphitic petals. Similar structures were later called as "carbon nanowall" [54, 55] and recently became more popular as "graphene" [56, 57]. In that sense, some people consider me as the first farmer of graphene as well [53].

When we observed by HRTEM, each purified MWCNT produced by H₂-arc discharge of pure graphite rod (Fig. 6(b)) shows characteristic feature with high-crystallinity MWCNTs with very narrow inner diameter [51, 58-62]. In the extreme case, we observed the smallest CNT of 0.4nm, the innermost tube of MWCNT [63, 64]. Later, the diameter of the thinnest possible CNT in such a MWCNT was found to be 0.3 nm [65]. Realization of a CNT diameter less than the usual inter-layer spacing of graphite (0.34 nm) is quite debatable [65]. An example of such MWCNT including 0.3 nm tube is shown in Fig. 8. In the region between A and A', such 0.3 nm innermost tube can be observed, and the intensity profile measured by densitometer between B and B' is inserted in Fig. 8.

The central weak peaks (0, 0') originate from 0.3 nm CNT, and the immediate next strong

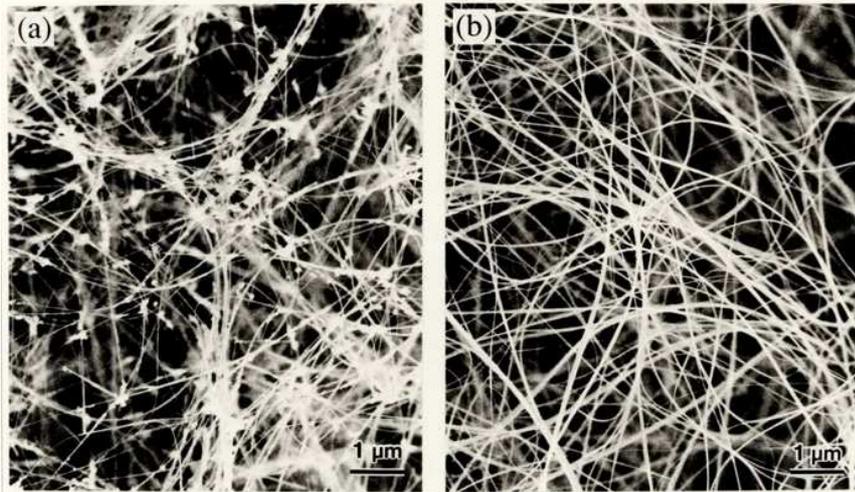


Fig. 6. SEM micrograph [52] (a) as grown. (b) purified

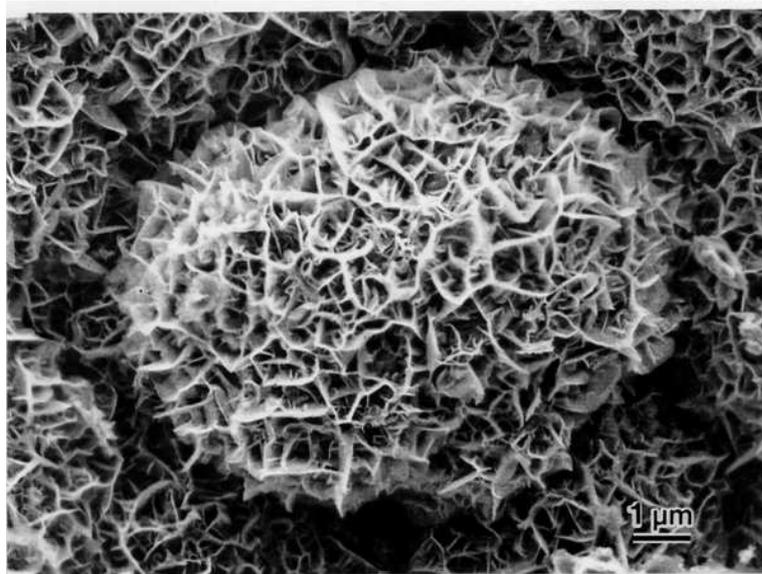


Fig. 7. SEM of petal-like graphene [53]

peaks ($1, 1'$) come from the innermost tube in MWCNT. The unusually high contrast results from the local structure distortion caused by the strong attraction between the 0.3 nm CNT and the innermost tube in the MWCNT. Raman spectra of these MWCNTs produced by H_2 -arc discharge of pure graphite rod show characteristic features in low and high frequency regions [59, 60, 66-70]. In Fig. 9(a) and (b), Raman spectra obtained by using Ar^+ laser (514.5 nm) are shown for low and high frequency regions, respectively [69, 70]. Three kinds of MWCNTs (A), (B) and (C) were produced by the same H_2 -arc discharge method but they show different spectra in low frequency region. For comparison, Raman spectrum of SWCNTs produced by APJ method [71] described later, and that of HOPG (highly oriented pyrolytic graphite [72])

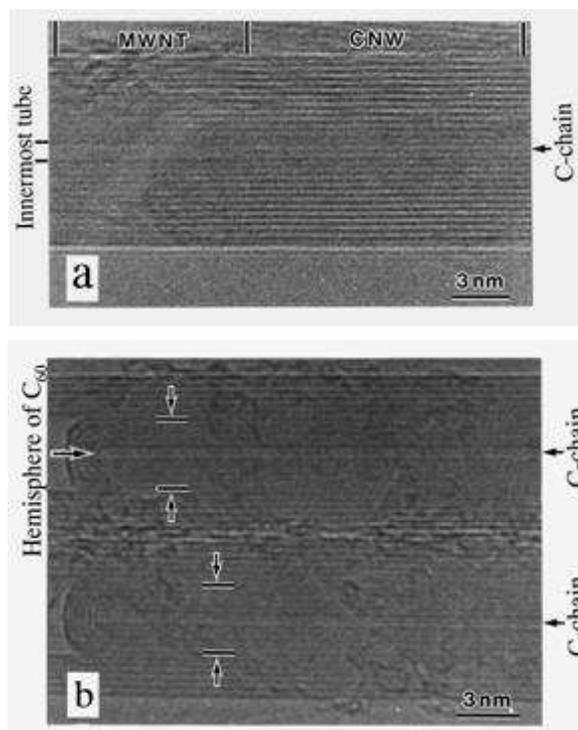


Fig. 10. HRTEM of CNW [75]

tube is 1.0 nm, but the diameter gradually decreases toward the right hand side and becomes 0.7 nm. In the region of 0.7 nm diameter of the innermost tube, we clearly see a black line in the center. Similarly in Fig. 10(b), two such lines are seen in the center of two adjacent MWCNTs. The contrast is considered due to linear carbon-chain at the center of each MWCNT. We call this C-chain-inserted MWCNT as "carbon nanowire (CNW)" [75]. A model of CNW is shown in Fig. 11.

One more memorabilia is that the thinnest innermost MWCNT of 0.3 nm shown in Fig. 8 and CNW shown in Fig. 10(a) are obtained from the adjacent parts of the same MWCNT. This peculiarity may be attributed to two facts. Firstly, the temperature of H₂ arc plasma is higher than He arc plasma in the same condition. And second, H₂ (being non-inert) makes the arc plasma more reactive. Some carbon species are captured inside MWCNTs, and they grow to thinnest tube or carbon chain depending on the size of the innermost tube. Specialized points in Raman spectra of MWCNTs produced by H₂-arc discharge are that new Raman peaks near 1850 cm⁻¹ appear [59, 67, 68, 75]. In usual carbon and graphite system, such Raman peak near 1850 cm⁻¹ can't be expected by any second-order harmonic or combination mode in sp² carbon allotropes [76]. Only such high frequency mode near 2000 cm⁻¹ can be expected for the stretching mode of 1D linear carbon chain [77]. As the length of the linear carbon chain becomes longer, the Raman peak position decreases [77].

To check the contribution of H-atom itself for the new Raman peak, we replaced the H₂ gas by D₂ gas, and obtained Raman spectra shown in Fig. 12. Nothing change of peak position G-band and new peaks (1830 and 1858 cm⁻¹) were observed by replacing H₂ gas to D₂ gas

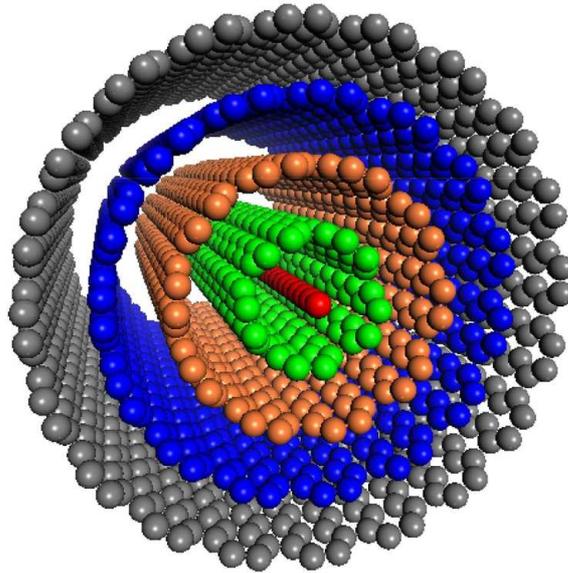


Fig. 11. Model of CNW [75]

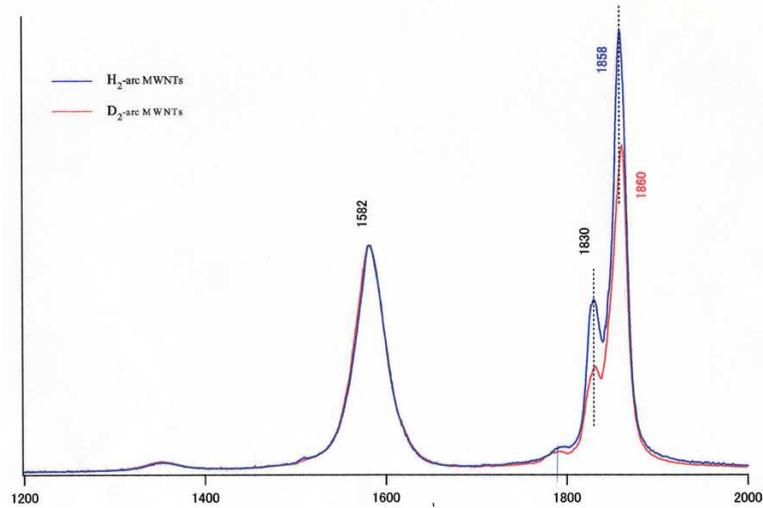


Fig. 12. Raman spectra of MWCNTs

[78, 79]. Therefore, we conclude that the new Raman peaks near 1850 cm^{-1} appears as the stretching mode of CNW [75], depending carbon atoms only. These new Raman peaks are reported by other group also in MWCNTs produced by He-arc discharge [80]. Electric resistance of each MWCNT produced by H_2 -arc discharge was measured by using micro-manipulator system [60, 61]. Temperature dependence of the electric resistance is shown in Fig. 13. Both types of MWCNT with semiconducting behavior (high resistance; decreasing with the temperature increase) and metallic behavior (low resistance; increasing with the temperature increase) were

observed as anticipated theoretically [81, 82]. This study indicates that our MWCNTs specimen contain both metallic and semiconducting CNTs.

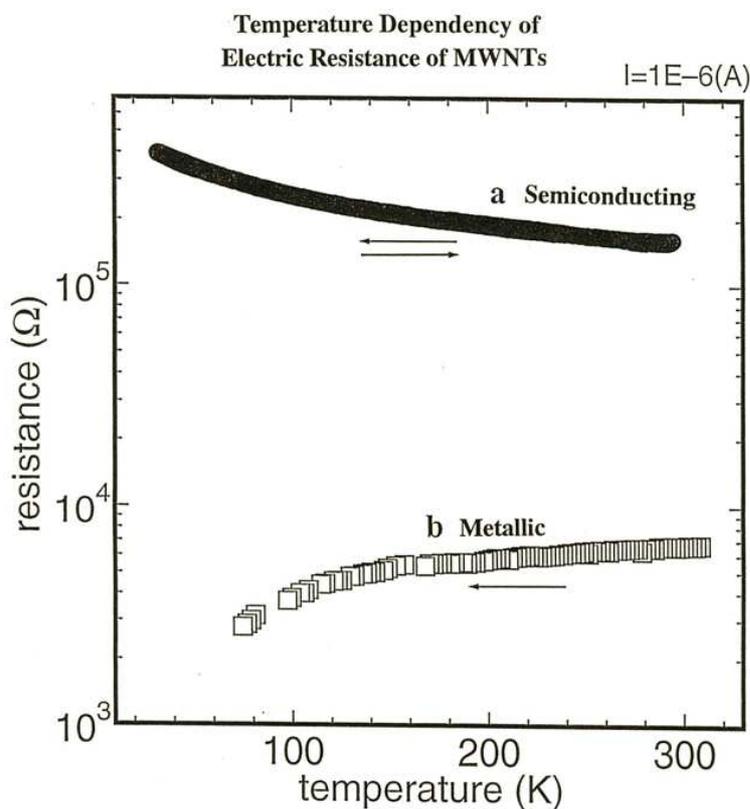


Fig. 13. Electric resistance [68]

4. Production of SWCNTs by APJ Method

The first specimens of SWCNTs also produced by DC arc discharge using anode including metal catalyst (Fe or Co), but the first production yield was very little as observed in TEM images [3, 4]. The yield of SWCNTs greatly increased by using binary metals (Ni and Y) in the anode [48]. By DC arc discharge in He (500torr), the SWCNTs were obtained in the cathode collaret and the web in the evaporation chamber [48]. The SWCNTs did not exist in the normal cathode deposit as in the MWCNTs case. When we evaporated the anode including binary metal catalyst by normal arc apparatus shown in Fig. 2, nearly half of the evaporated carbon from the anode gets deposited on the cathode end which became MWCNTs and didn't contain any SWCNTs. In order to decrease the cathode deposit and increase the SWCNT soot generation in DC arc discharge, we made the two electrodes inclined at 30 degrees (instead of usual 180 degrees). Under this configuration, the arc plasma between the two electrodes occurs like a jet. Therefore we named this as arc plasma jet (APJ) method [71]. By the APJ method, the cathode deposit could be remarkably decreased and increased the soot including SWCNT. The production rate

of soot including SWCNTs is the order of 1 g/min.

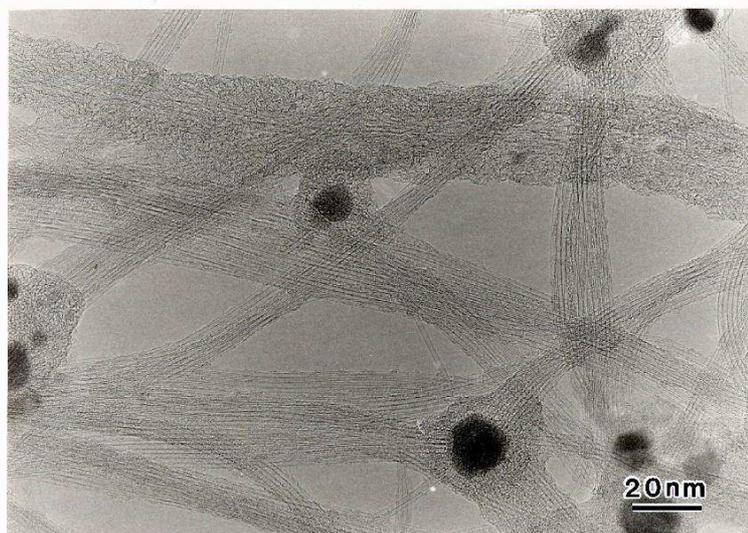


Fig. 14. HRTEM of APJ-SWCNTs [71]

An example of HRTEM micrographs of the produced soot is shown in Fig. 14. In the micrograph we can observe a large number of bundles of SWCNTs, and catalyst Ni particles of the order of 20nm. Each Ni particle is covered with thick (the order of 10 nm) amorphous carbon [71]. If we want to use this SWCNTs prepared by APJ method, it is necessary to purify. Amorphous carbon should be removed first, and then Ni particles are dissolved by HCl. Under this purification process, SWCNTs also heavily damaged and fade out, and we can get pure SWCNTs less than 10%. Purification of SWCNTs is a tedious process and the CNT quality gets deteriorated after chemical purification. Hence, to eliminate (or minimize) the purification step, it is necessary to grow high-purity SWCNTs in the as-grown condition.

5. Production of SWCNTs by FH-arc Method

In order to get easily purifiable SWCNTs, we refined the arc evaporation method. To inhibit the production of amorphous carbon, H_2 gas was introduced as in the case of MWCNTs. However, for pure H_2 gas, the flame of arc becomes to be unstable, and added inert gas. As easily removable metal catalyst, Fe was used. Because of the importance of the use Fe catalyst and H_2 gas, we call this arc method as "Ferrum-Hydrogen (FH) arc method" [83]. Evaporation of the graphite anode (with 1 at % Fe), we get long webs of SWCNTs as a result of 5-6 minute arc discharge (Fig. 15). A long cathode was put on the upper side in Fig. 2, and the web of SWCNTs grows from the lower tip of the cathode to the ceiling of the chamber. The total length of the SWCNTs web is almost 30 cm, of course is the length of SWCNTs bundles and not each SWCNT [83].

The electron micrographs of SWCNTs prepared by FH-arc method are shown in Fig. 16(a) – (d). Fig. 16(a) is a TEM micrograph of as grown SWCNTs, network of SWCNTs bundle and black particles of Fe catalyst can be observed [83]. Fig. 16(b) is a HRTEM micrograph of SWCNTs bundle and catalyst Fe particles. The size of catalyst Fe particles is the order of 10 nm, and each



Fig. 15. SWCNTs net produced by FH-arc [83]

Fe particle is covered with thin amorphous carbon thinner than 5 nm. Because the thickness of amorphous carbon is fairly thin, removing them by heating is easy and then Fe particles can be resolved by HCl. After the purification, SEM and TEM observation has been done as shown in Figs. 16(c) and (d). It turns out that Fe particles have been almost removed.

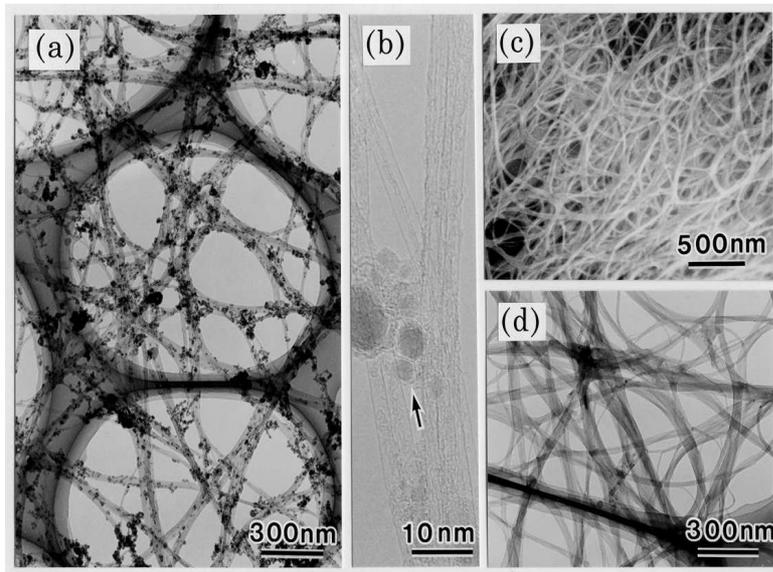


Fig. 16. SWCNTs[83]. (a), (b): as grown. (c), (d):purified

As-produced SWCNTs web has very low green density. When it has packed softly in a one

liter bottle, the mass is only one gram, namely the green density of SWCNTs web is 0.001 g/cm^3 , as shown in Fig. 17 [84]. The mass production of SWCNTs by FH-arc method has been tried by optimization of atmospheric gas using heavy inert gas (Xe or Kr)[85] and developing the different kinds of Fe-doped carbon electrodes [86]. Optical emission spectroscopy of arcing state for FH-arc method also have been done [87]. C_2 radial emission (Swan band) was measured to evaluate the temperature (maximum 6,000 K) and concentration fields (C_2 column density; $1.2 \times 10^{16} \text{ cm}^{-2}$) in a carbon arc plasma during SWCNTs production [87].

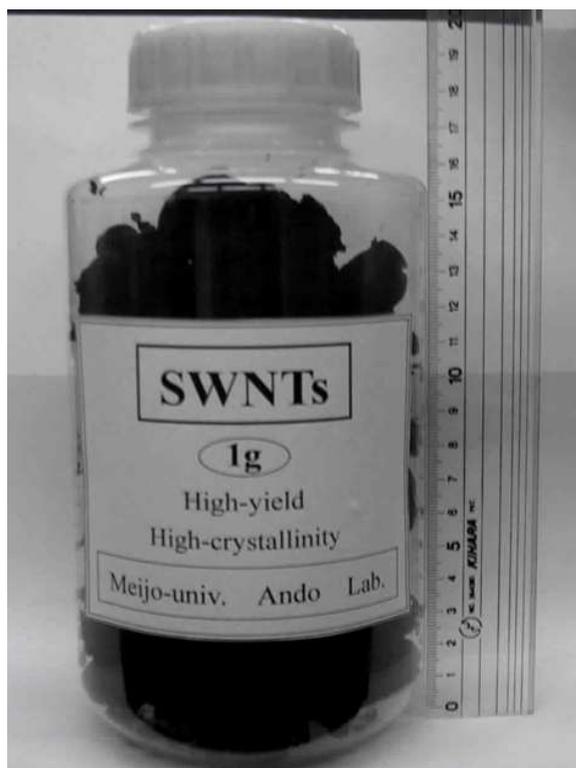


Fig. 17. Bottled SWCNTs [84]

Many kinds of purification process of SWCNTs have been proposed [88, 89]. Moreover, it was verified that the adding of Fe particles as catalyst is effective for the liquid-phase purification of SWCNTs using H_2O_2 [90]. The smaller size of Fe particles attributes to better catalytic activity. This result could be applied for the purification of SWCNTs produced by APJ method [91]. 10% addition of as-grown FH-arc SWCNTs, which originally includes Fe nanoparticles, purify APJ-SWCNTs effectively.

6. Production of DWCNTs by Arc Discharge

As an extension of SWCNTs, double-walled carbon nanotubes (DWCNTs) also were made by arc discharge [92, 93]. The existence of DWCNTs were confirmed by HRTEM and RBM in Raman spectra. DWCNTs are expected mechanically strong than SWCNTs by their structure, application to the field emission also is expected. The first stage of DWCNTs growth could

be observed [94] in thick SWCNTs produced by arc discharge of the anode including tri-metal catalyst (Fe-Ni-Co) in the ambient gas $\text{H}_2(500\text{torr}) + 1\%\text{H}_2\text{S}$.

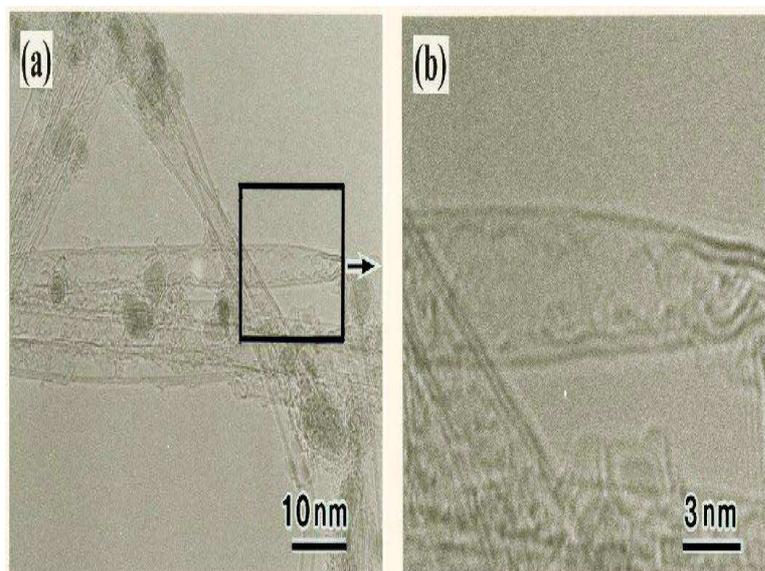


Fig. 18. HRTEM of a first stage of DWCNT production. (b) Enlarged HRTEM [94]

The addition of $1\%\text{H}_2\text{S}$ also essential for the production of thick SWCNTs and DWCNTs [91]. An HRTEM micrograph of DWCNT growth is shown in Fig. 18(a) and its enlarged one in Fig. 18(b). Consideration on the growth of DWCNTs prepared by arc discharge has been done by Saito et al. [95]. They supported our conclusion that the addition of sulfur to Fe, Co, Ni catalysts, and the presence of hydrogen in atmospheric gas are indispensable for selective formation of DWCNTs.

Summary

Table 1. Growth conditions and structure properties of CNTs produced by arc discharge method in Ando laboratory

Kind of CNT	Method	Catalyst	Ambient gas	Produced position	Item	Number of layers	Diameter of tube (nm)	Length of tube (μm)
SWCNT	APJ	Ni4%Y1%	He: 500torr	whole chamber	mass production of SWCNTs	1	1.2- 1.5	- 2- 10
	FH- arc	Fe1%	H_2+Ar : 200torr	whole chamber	macroscopic web of SWCNTs	1	0.8- 1.5	- 2- 10
DWCNT	normal DC arc	Fe0.25%+Ni0.9%+Co0.9%	$\text{H}_2+\text{H}_2\text{S}$ 1% 500torr	whole chamber	thick SWCNTs and DWCNTs	2	1.4- 4	- 2- 10
MWCNT	normal DC arc	none	H_2 : 30- 100torr	cathode deposit	thin inner tube & carbon nanowire	3- 30	10- 30	> 10
		Y or Sc or La	He: 500torr	cathode deposit	mass production of MWCNTs	10- 40	20- 40	> 10

In this brief review, I have stated the inside story of the discovery of CNTs. The growth conditions and structure properties of CNTs produced by arc discharge method in our laboratory are summarized in Table 1.

This science story illustrates the inside world of CNTs synthesized in hydrogen arc discharge. My 30-year-old arc-discharge chamber, that gave birth to the discovery specimens of CNT, has maintained its glory by producing beautiful carbon nanowalls, the smallest MWCNT (0.4 nm), the wonderful carbon chain inserted in 0.7 nm tubes, and then the sensational 0.3 nm MWCNT. Macroscopic webs of SWCNTs were also produced by this old arc chamber; and it is still working fine. But please don't ask me what next! I think, the answer lies in the hands of the next-generation CNT researchers.

References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature*, **318**(1985), 162.
- [2] S. Iijima, *Nature*, **354**(1991), 56.
- [3] S. Iijima, T. Ichihashi, *Nature*, **363**(1993), 603.
- [4] D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, *Nature*, **363**(1993), 605.
- [5] R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998.
- [6] Y. Saito, S. Bandow, *Basis of Carbon Nanotubes*, Corona-shya, Tokyo, 1998 (in Japanese).
- [7] S. Iijima, *Challenge of Carbon Nanotubes*, Iwanami-Shyoten, Tokyo, 1999 (in Japanese).
- [8] D. Tománek, R.J. Enbody, *Science Application of Nanotubes*, Kluwer Academic/ Plenum Publishers, New York, 2000.
- [9] M.S. Dresselhaus, G. Dresselhaus, Ph. Avouris, *Carbon Nanotubes*, Springer-Verlag, Berlin, 2001.
- [10] T.W. Ebbesen, *Physics Today*, **49**(1996), 26.
- [11] Y. Ando, *Encyclopedia of Nanoscience Nanotechnology*, edited by H.S. Nalwa, *Amer. Scie. Publish.*, **1**(2004), 603.
- [12] M. Terrones, *Int. Mater. Rev.*, **49**(2004), 325.
- [13] Y. Ando, X. Zhao, T. Sugai, M. Kumar, *Materials Today*, **7**(2004), 22.
- [14] Y. Ando, X. Zhao, *New Diamond Front. Carbon Tech.*, **16**(2006), 123.
- [15] Y. Ando, S. Iijima, *Jpn. J. Appl. Phys.*, **32**(1993), L107.
- [16] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tománek, J.E. Fisher, R.E. Smalley, *Science*, **273**(1996), 483.
- [17] M. José-Yacamán, M. Miki-Yoshida, L. Rendon, J.G. Satiesteban, *Appl. Phys. Lett.*, **62**(1993), 202.
- [18] Y. Ando, M. Ohkohchi, *J. Cryst. Growth*, **60**(1982), 147.

-
- [19] W. Krätschmer, K. Fostiropoulos, D.R. Huffman, *Chem. Phys. Lett.*, **170**(1990), 167.
- [20] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, *Nature*, **347**(1990), 354.
- [21] S. Iijima, T. Ichihashi, Y. Ando, *Nature*, **356**(1992), 776.
- [22] P.M. Ajayan, S. Iijima, *Nature*, **358**(1992), 23.
- [23] S. Iijima, P.M. Ajayan, T. Ichihashi, *Phys. Rev. Lett.*, **69**(1992), 3100.
- [24] A. Oberlin, M. Endo, T. Koyama, *Carbon*, **14**(1976), 133.
- [25] L.V. Radushkevich, V.M. Lukyanovich, *Zhurn Fisic Chim.*, **26**(1952), 88.
- [26] W.R. Davis, R.J. Slawson, G.R. Rigby, *Nature*, **171**(1953), 756.
- [27] M. Monthieux, V.L. Kuznetsov, *Carbon*, **44**(2006), 1621.
- [28] H. Shinohara, *Science of Nano Carbons*, Blue Backs, Koudansya, Tokyo, 2007 (in Japanese).
- [29] R. Uyeda, *J. Cryst. Growth*, **45**(1978), 485.
- [30] Y. Ando, R. Uyeda, *J. Amer. Ceram. Soc.*, **64**(1981), C-12.
- [31] X. Zhao, M. Wang, M. Ohkohchi, Y. Ando, *Bull. Res. Inst. Meijo Univ.*, **1**(1996), 7.
- [32] Y. Saito, M. Inagaki, H. Shinohara, H. Nagashima, M. Ohkohchi, Y. Ando, *Chem. Phys. Lett.*, **200**(1992), 643.
- [33] M. Ohkohchi, Y. Ando, *J. Japan Ceramic Soc.*, **94**(1986), 26 (in Japanese).
- [34] Y. Saito, K. Kurosawa, H. Shinohara, S. Saito, A. Oshiyama, Y. Ando, T. Noda, *J. Phys. Soc. Japan*, **60**(1991), 2518.
- [35] Y. Saito, N. Suzuki, H. Shinohara, Y. Ando, *Jpn. J. Appl. Phys.*, **30**(1991), 2857.
- [36] Y. Saito, H. Shinohara, M. Kato, H. Nagashima, M. Ohkohchi, Y. Ando, *Chem. Phys. Lett.*, **189**(1992), 236.
- [37] H. Shinohara, H. Sato, M. Ohkohchi, Y. Ando, T. Kodama, T. Shida, T. Kato, Y. Saito, *Nature*, **357**(1992), 52.
- [38] H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando, Y. Saito, *J. Phys. Chem.*, **97**(1993), 4259.
- [39] S. Iijima, *J. Cryst. Growth*, **50**(1980), 675.
- [40] S. Iijima, *J. Phys. Chem.*, **91**(1987), 3466.
- [41] Y. Ando, *Jpn. J. Appl. Phys.*, **32**(1993), L1342.
- [42] T.W. Ebbesen, P.M. Ajayan, *Nature*, **358**(1992), 220.
- [43] Y. Ando, *Fullerene Sci. Tech.*, **2**(1994), 173.
- [44] X. Zhao, M. Wang, M. Ohkohchi, Y. Ando, *Jpn. J. Appl. Phys.*, **35**(1996), 4451.

- [45] M. Wang, X. Zhao, M. Ohkohchi, Y. Ando, *Fullerene Sci. Tech.*, **4**(1996), 1027.
- [46] M. Ohkohchi, Y. Ando, S. Bandow, Y. Saito, *Jpn. J. Appl. Phys.*, **32**(1993), L1248.
- [47] M. Ohkohchi, X. Zhao, M. Wang, Y. Ando, *Fullerene Sci. Tech.*, **4**(1996), 977.
- [48] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.L. de la Chapelle, S. Lefrant, P. Deniard, R. Lée, J.E. Fisher, *Nature*, **388**(1997), 756.
- [49] Y. Tai, K. Inukai, T. Osaki, M. Tazawa, J. Murakami, S. Tanemura, Y. Ando, *Chem. Phys. Lett.*, **224**(1994), 118.
- [50] X.K. Wang, X.W. Lin, V.P. Dravid, J.B. Ketterson, R.P.H. Chang, *Appl. Phys. Lett.*, **66**(1995), 2430.
- [51] X. Zhao, M. Ohkohchi, H. Shimoyama, Y. Ando, *J. Cryst. Growth*, **198/199**(1999), 934.
- [52] Y. Ando, X. Zhao, M. Ohkohchi, *Jpn. J. Appl. Phys.*, **37**(1998), L61.
- [53] Y. Ando, X. Zhao, M. Ohkohchi, *Carbon*, **35**(1997), 153.
- [54] Y. Wu, P. Qiao, T. Chong, Z. Shen, *Adv. Mater.*, **14**(2002), 64.
- [55] M. Hiramatsu, M. Hori, *Jpn. J. Appl. Phys.*, **45**(2006), 5522.
- [56] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos, A.A. Firsov, *Nature*, **438**(2005), 197.
- [57] P. Blake, E.W. Hill, A.H. Castro Neto, K.S. Novoselov, D. Jiang, R. Yang, T.J. Booth, A.K. Geim, *Appl. Phys. Lett.*, **91**(2007), 063124.
- [58] X. Zhao, M. Ohkohchi, M. Wang, S. Iijima, T. Ichihashi, Y. Ando, *Carbon*, **35**(1997), 775.
- [59] X. Zhao, Y. Ando, *Jpn. J. Appl. Phys.*, **37**(1998), 4846.
- [60] Y. Ando, X. Zhao, H. Shimoyama, G. Sakai, K. Kaneto, *J. Inorganic Materials*, **1**(1999), 77.
- [61] K. Kaneto, M. Tsuruta, G. Sakai, X. Zhao, Y. Ando, *Synthetic Metals*, **103**(1999), 2543.
- [62] Y. Ando, X. Zhao, H. Shimoyama, *Carbon*, **39**(2001), 569.
- [63] L.-C. Qin, X. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando, S. Iijima, *Nature*, **408**(2000), 50.
- [64] L.-C. Qin, X. Zhao, K. Hirahara, Y. Ando, S. Iijima, *Chem. Phys. Lett.*, **349**(2001), 389.
- [65] X. Zhao, Y. Liu, S. Inoue, T. Suzuki, R.O. Jones, Y. Ando, *Phys. Rev. Lett.*, **92**(2004), 125502.
- [66] H. Kataura, Y. Achiba, X. Zhao, Y. Ando, *Mat. Res. Soc. Symp. Proc.*, **593**(2000), 113.
- [67] Y. Ando, X. Zhao, H. Kataura, Y. Achiba, K. Kaneto, S. Uemura, S. Iijima, *Trans. Mater. Res. Soc. Japan*, **25**(2000), 817.
- [68] Y. Ando, X. Zhao, H. Kataura, Y. Achiba, K. Kaneto, M. Tsuruta, S. Uemura, S. Iijima, *Diamond Rel. Mater.*, **9**(2000), 847.

-
- [69] X. Zhao, Y. Ando, L.-C. Qin, H. Kataura, Y. Maniwa, R. Saito, *Chem. Phys. Lett.*, **361**(2002), 169.
- [70] X. Zhao, Y. Ando, L.-C. Qin, H. Kataura, Y. Maniwa, R. Saito, *Appl. Phys. Lett.*, **81**(2002), 2550.
- [71] Y. Ando, X. Zhao, K. Hirahara, K. Suenaga, S. Bandow, S. Iijima, *Chem. Phys. Lett.*, **323**(2000), 580.
- [72] L.C.F. Blackman, A.R. Ubbelohde, *Proc. Roy. Soc. A*, **266**(1962), 20.
- [73] A.M. Rao, E. Richter, S. Bandow, B. Chase, P.C. Eklund, K.A. Williams, S. Fang, K.R. Subbaswamy, M. Menon, A. Thess, R.E. Smalley, G. Dresselhaus, M.S. Dresselhaus, *Science*, **275**(1997), 187.
- [74] S. Bandow, S. Asaka, Y. Saito, A.M. Rao, L. Grigorian, E. Richter, P.C. Eklund, *Phys. Rev. Lett.*, **80**(1998), 3779.
- [75] X. Zhao, Y. Ando, Y. Liu, M. Jinno, T. Suzuki, *Phys. Rev. Lett.*, **90**(2003), 187401.
- [76] V.W. Brar, Ge.G. Samsonidze, M.S. Dresselhaus, G. Dresselhaus, R. Saito, A.K. Swan, M.S. Ünlü, A. Jorio, *Phys. Rev. B*, **66**(2002), 155418.
- [77] J. Kürti, C. Magyar, A. Balázs, P. Rajczy, *Synth. Met.*, **71**(1995), 1865.
- [78] M. Jinno, S. Bandow, Y. Ando, *Chem. Phys. Lett.*, **398**(2004), 256.
- [79] M. Jinno, Y. Ando, S. Bandow, J. Fan, M. Yudasaka, S. Iijima, *Chem. Phys. Lett.*, **418**(2006), 109.
- [80] E. Cazzanelli, M. Castriota, L.S. Caputi, A. Cupolillo, C. Giallombardo, L. Papagno, *Phys. Rev. B*, **75**(2007), 121405.
- [81] N. Hamada, A. Sawada, A. Oshiyama, *Phys. Rev. Lett.*, **68**(1992), 1579.
- [82] R. Saito, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, *Appl. Phys. Lett.*, **60**(1992), 2204.
- [83] X. Zhao, S. Inoue, M. Jinno, T. Suzuki, Y. Ando, *Chem. Phys. Lett.*, **373**(2003), 266.
- [84] Y. Ando, X. Zhao, S. Inoue, T. Suzuki, M. Ohkohchi, *Trans. Mater. Res. Soc. Japan*, **30**(2005), 1193.
- [85] Y. Ando, X. Zhao, S. Inoue, T. Suzuki, T. Kadoya, *Diamond Rel. Mater.*, **14**(2005), 729.
- [86] X. Zhao, T. Kadoya, T. Ikeda, T. Suzuki, S. Inoue, M. Ohkohchi, Y. Takimoto, Y. Ando, *Diamond Rel. Mater.*, **16**(2007), 1101.
- [87] A. Huczko, H. Lange, M. Bystrzejewski, P. Baranowski, Y. Ando, X. Zhao, S. Inoue, *J. Nanosci. Nanotech.*, **6**(2006), 1.
- [88] A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodriguez-Macias, P.J. Boul, R.E. Smalley, *Appl. Phys. A*, **67**(1998), 29.
- [89] Y. Feng, G. Zhou, G. Wang, M. Qu, Z. Yu, *Chem. Phys. Lett.*, **375**(2003), 645.

- [90] X. Zhao, M. Ohkohchi, S. Inoue, T. Suzuki, T. Kadoya, T. Kitamura, T. Ikeda, Y. Ando, *Diamond Rel. Mater.*, **15**(2006), 1098.
- [91] T. Suzuki, K. Suhama, X. Zhao, S. Inoue, N. Nishikawa, Y. Ando, *Diamond Rel. Mater.*, **16**(2007), 1116.
- [92] J.L. Hatchison, N.A. Kiselev, E.P. Krinichnaya, A.V. Krestinin, R.O. Loutfy, A.P. Morawsky, V.E. Muradyan, D.N. Zakharov, *Carbon*, **39**(2001), 761.
- [93] L. Li, F. Li, C. Liu, H.-M. Cheng, *Carbon*, **43**(2005), 623.
- [94] Y. Ando, X. Zhao, K. Hirahara, S. Iijima, Nanonetwork Materials, edited by S. Saito et al., 2001 AIP, CP590, 7.
- [95] Y. Saito, T. Nakabira, S. Uemura, *J. Phys. Chem. B*, **107**(2003), 931.

Углеродная нанотрубка: история из первых уст Йошинори Андо

Йошинори Андо

Углеродные нанотрубки (CNTs) были удивительным образом получены как побочный продукт фуллеренов в дуговом разряде при постоянном токе (DC), а сегодня они являются наиболее востребованным материалом в нанотехнологии. Этот краткий обзор я начну с истории открытия CNTs и остановлюсь на углеродных нанотрубках, полученных методом дугового испарения в водороде, малоизученных вне стен моей лаборатории. Испарение графитовых электродов в дуговом разряде при DC в среде водорода приводит к получению хорошо упорядоченных многостенных углеродных нанотрубок (MWCNTs), находящихся в осадке на катоде. Полученные MWCNTs имеют очень маленький внутренний диаметр. Спектр комбинационного рассеяния MWCNTs показывает высокую интенсивность в диапазоне G, необычную высокочастотную радиальную "дышащую" моду 570 см^{-1} и новый характерный пик около 1850 см^{-1} . Также в центре MWCNT были получены интересные углеродные нанопровода (CNWs), состоящие из линейной углеродной цепочки. Дуговое испарение графита, содержащего металлический катализатор, приводит к получению сетей одностенных углеродных нанотрубок (SWCNTs) макроскопического размера, находящихся во всей камере. Два вида дуговых методов были разработаны для получения SWCNTs: дуга из плазменного факела (APJ) и железно-водородная дуга (FH). Обсуждены некоторые новые методы очищения полученных SWCNTs. В конце обзора также описаны двухстенные углеродные нанотрубки (DWCNTs).

Ключевые слова: углеродные нанотрубки, методы синтеза.