A super-growth method for single-walled carbon nanotube synthesis

— Development of a mass production technique for industrial application —

Kenji HATA

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More than 20 years have passed since Dr Sumio Iijima discovered single-walled carbon nanotubes (CNTs). Development of this material is still an active area of research, world-wide, because the expected high electric and heat conductivity and mechanical strength properties are difficult to obtain with other existing materials. However, low growth efficiency of single-walled CNTs has made the cost of production high compared to that of multi-walled CNTs. Consequently, commercialization of single-walled CNTs has taken longer to develop than multi-walled CNTs. To address this problem, a super-growth process was developed at the National Institute of Advanced Industrial Science and Technology (AIST) that uses an innovative chemical vapor deposition (CVD) method. The super-growth method opens the door to a range of industrial applications widely. This report describes the development of this process for industrial scale, mass production of high quality single-walled CNTs, with commercialization in mind, from the perspective of business-academia collaboration.

Keywords : Super-growth CVD, single-walled CNT, element technology integration, industrial application, business-academia collaboration

1 Background of research

1.1 Introduction of the single-walled CNT

A single-walled carbon nanotube (single-walled CNT, Fig. 1) is composed of a structure in which graphene, which is composed of carbon atoms aligned in a planar honeycomb structure, is rolled into a one-walled cylinder. Ever since the discovery of single-walled CNTs was reported by Dr. Sumio Iijima[1] and the IBM group[2] in 1993, it was experimentally shown to possess electroconductivity, thermal conductivity, and mechanical strength that could not be achieved by conventional materials, and much R&D was conducted with fervor. The application of single-walled CNTs spreads widely over chemical, electrical, and mechanical fields, and as a prime nanotechnology material, researchers around the world have been engaging in fierce competition since its discovery 20 years ago. Figure 2 shows the change in the number of papers on CNTs. Since its discovery 20 years ago, the number of CNT papers has been on the rise. The number of CNT researchers is gradually decreasing since the research boom for CNTs has somewhat settled, but the number of papers is increasing, and this shows that CNTs have spread widely as research material and the number of CNT users has increased. CNT is used for research that generates over 8,000 papers annually, and this is a testament to the fact that CNTs have multiple characteristics that can be applied to various uses.

While academic research of CNTs is enthusiastically conducted, single-walled CNTs are used in a limited manner despite the competitive R&D around the world since its discovery 20 years

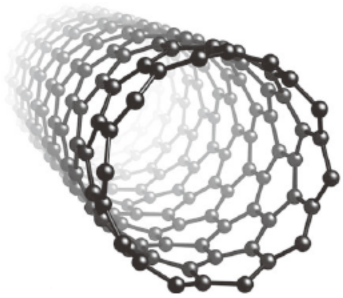

Fig. 1 Single-walled CNT

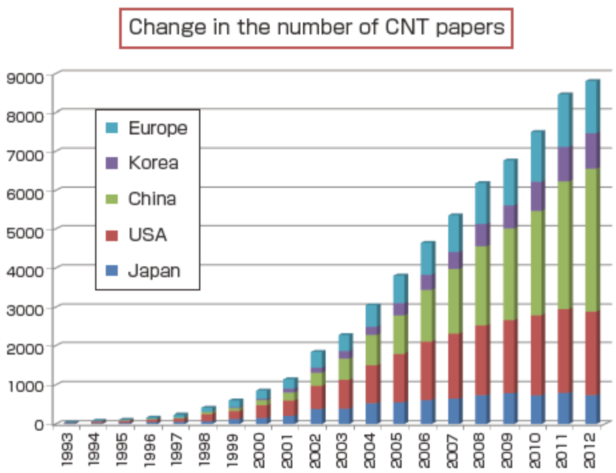

Fig. 2 Change in the number of CNT papers

CNT-Application Research Center, AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan ＊ E-mail: kenji-hata@aist.go.jp

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ago, and one cannot say that it has been industrialized. The reason is the low growth efficiency of the synthesis of single-walled CNTs. Since the production efficiency is extremely low, the cost is extremely high. The price of the most common commercial single-walled CNT is several tens of thousands of yen per gram, and this price range puts it outside the scope of industrial material. Compared to single-walled CNTs, the multi-walled CNTs have high growth efficiency, are commercially produced, are sold for about five thousand to ten thousand yen per kilogram, and are distributed widely around the world.

1.2 Conventional synthesis methods of CNTs and their issues

Some of the synthesis methods of single-walled CNTs include the laser abrasion method,[3] the electric arc method,[4] and the chemical vapor deposition (CVD) method[5] (Fig. 3). Among these methods, only the CVD method was applied to industrial mass production. For the CVD method, industrial mass production was realized for multi-walled CNTs using the conventional mass production processes that use rotary kilns and fluid bed furnaces, and several commercial plants around the world with production capacity of several hundred tons per year are in operation. However, compared to multi-walled CNTs, single-walled CNTs had narrower diameter and necessitated precise catalyst control. Moreover, the catalyst tended to become deactivated extremely easily, and it was difficult to synthesize at a high yield. When single-walled CNTs were synthesized with the conventional CVD method, the catalyst lifespan was a few minutes, the catalyst activity was several percent, and the growth efficiency was extremely low. As a result, the major problem was the large amount of catalyst metal particles that remained in the CNTs as impurities. Therefore, before actually using the single-walled CNTs, they had to undergo refinement to remove catalyst impurities. This refinement method consisted of several steps of complicated chemical processes such as oxidation at high temperature and acid treatment, and not only were they expensive, but they also would damage the single-walled CNTs.

	Yield	Cost	Purity	Quality
Electric arc	Poor	Poor	Poor	Excellent
Laser ablation	Poor	Poor	Poor	Excellent
Supported catalyst CVD fluid bed furnace	Excellent (3D)	Excellent	Poor	Poor
Vapor fluid method Short Growth Time (e.g. HiPco)	Good(2D)	Moderate	Poor	Good
Vapor fluid method Low Density (e.g. eDips)	Moderate (2D)	Moderate	Good	Excellent
Super-growth	Good(2D)	Moderate	Excellent	Moderate

Super-growth is a synthesis method that fulfills the demands of yield, cost, purity, and quality

Fig. 3 Comparison of the synthesis methods for single-walled CNTs

2 Core technology of the research

2.1 Super-growth method

An innovative CVD method that solved all the technological issues of single-walled CNTs was developed at the National Institute of Advanced Industrial Science and Technology (AIST) in 2004. This was the super-growth method[6] (Fig. 4).

The super-growth method is a method where the activity and lifespan of the catalyst are greatly improved by adding trace amount of water to a regular vapor synthesis atmosphere, and thereby greatly increasing the growth efficiency. By adding trace amount of water, the catalyst activity that was normally a few percent increased to over 84 %[7] and the catalyst lifespan of several minutes extended to over several tens of minutes to an hour.

In the super-growth method, the CNTs can be synthesized most efficiently from iron catalysts on the substrate coated with alumina catalyst supports. It enables the synthesis of "forests" or the long CNT structures aligned vertically on the substrate.

With this super-growth method, the improvement of growth efficiency of several hundred times was achieved compared to the conventional CNT synthesis methods such as laser ablation, electric arc, HiPCo process, alcohol CVD, or vapor fluid methods.

For example, the catalyst efficiency of the super-growth method reached 50,000 % by product/catalyst weight ratio, and this was an improvement of several hundred times compared to the conventional CNT synthesis methods (laser ablation 500 %, HiPCo 300 %, alcohol CVD 800 %, and vapor fluid 100 %). The dramatic decrease of the amount of catalysts used indicated large manufacturing cost reduction in the future using this growth method.

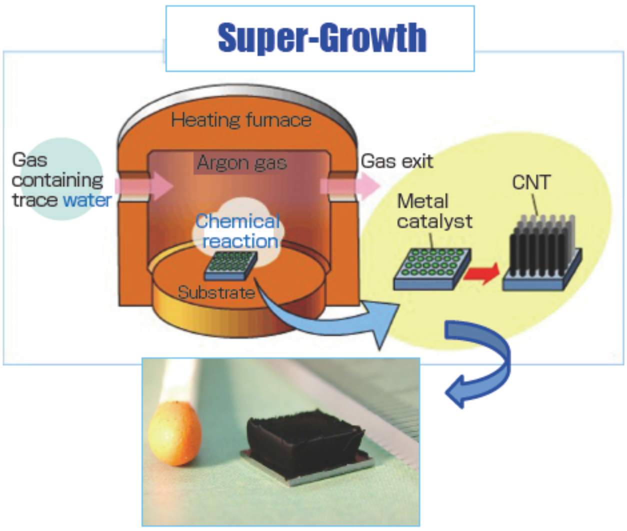

Fig. 4 Super-growth method

As of 2004 when the method was published, the vertically aligned single-wall CNT structure grew to 1.5 mm length in 10 min. This was an improvement of 500 times in length and 3,000 times in time efficiency compared to the world record at the time. The high-speed growth by the super-growth method showed that large amount of CNTs could be synthesized in a short time, and the road to full commercial production of single-walled CNTs was paved.

Moreover, the single-walled CNT forests could be easily sliced off from the substrate using a blade, just like harvesting rice. The catalyst was firmly attached to the substrate, and breakage occurred at the interface of the catalyst and CNTs, and as a result, the CNTs and the catalyst could be separated. Therefore, the amount of catalysts that was mixed in the CNT products was minute, and the CNTs with carbon purity 99.98 % or more could be manufactured on the spot. This purity was 1/2,000 of the impurity concentration in the single-walled CNTs manufactured by the HiPCo method that is most widely used today. The ability to synthesize CNT products with high purity and without need of a refinement process was a major advantage compared to the conventional synthesis method in using the single-walled CNTs as industrial material.

2.2 Research policy that set the direction and my thoughts

Since the super-growth method was published in November 2004, I questioned myself which research to do next. I thought that ideas and what could be done were limitless, including clarification of the mechanism of water addition or the creation of some bizarre CNT structures. In fact, most of the research topics that I conceived at the time or were brewing in the laboratory were published in illustrious academic journals a few years later. The super-growth method opened the possibilities to various new kinds of research.

Although I was surrounded by much exciting research potential, I did not choose my research topics at whim. That was because I gave myself some policies in selecting the research that I should engage in the future. The policies were:

- to engage in research that would be useful to the world,
- to engage in research that would become industrial technology that may support Japan in 10 or 20 years from now, although it may be dull at the moment,
- to engage in research of which I can appreciate the results at the end of my life.

Why did I give myself such research policies? This was because I had a bitter experience when I was working on surface science research. Around 2000, I was conducting research on atomic structure analysis of semiconductor surfaces using the scanning tunneling microscope at Tsukuba University, and I went to the American Vacuum Society (the largest and most authoritative society in the field of surface science) to give a lecture presentation of my greatest finding during the preceding few years (this was later published in *Physical Review Letter*).[8] In a lecture hall having seating capacity of 300 that was normally filled with several hundred people, there were only ten people. Most of them were Japanese. Right before this event, the National Science Foundation (NSF) that was the research funding agency in the United States suddenly decided to cut funds to the surface science field, and researchers left this field like an ebbing tide. Until that moment I thought science was the pursuit of absolute truths to clarify nature's mechanism and therefore it had absolute value. My experience in the US taught me that in the real world there is research that goes in and out of trend, and research is not evaluated based on absolute value.

From this experience in the US, I began to think about engaging in research that was not affected by trend, and wished to do research where the results are ultimately returned and become useful in society, rather than engaging in research to clarify the ways of nature. The aforementioned three research policies were the expression of my thoughts in a somewhat abstract form.

This abstract wish became a specific goal in a slide (Fig. 5) that was used for presentation for visitors from the Ministry of Economy, Trade and Industry (METI) that I was in charge of in March 2005, right after the press release of the super-growth method. Someday, when I go home, my elderly mother will be using a product that contains the super-growth CNTs, and I want to tell her, "Oh, mom. This product has CNTs in it that we developed at Tsukuba." To say this sentence became my personal goal as a researcher. This is because when I say these words, there should be a giant CNT industry in Japan, and our research will be contributing considerably in society. I used this slide repeatedly on visits and in lectures, and I must have re-used it several hundred times, as it represents my research philosophy and goal. In retrospect, this thought and wish were the source of my power to overcome all difficulties that came one after the other, and allowed me to realize the commercial production of the super-growth method.

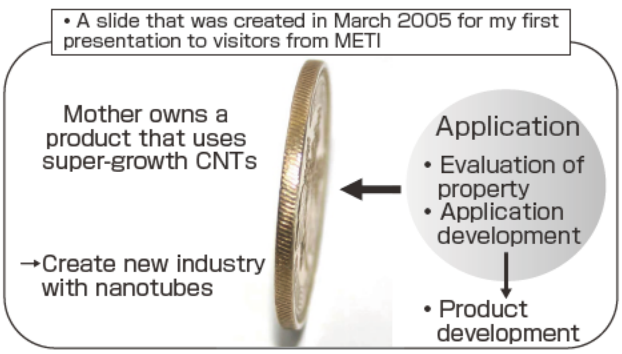

Fig. 5 Personal goal

In my research policy, the final research topic was "to develop mass production technology by the super-growth method and to make available single-walled CNTs as industrial material." Assuming a synthesis furnace of a length of 20 m and a width of 1 m to continuously manufacture single-walled CNTs by the super-growth method, the production volume was calculated at 10 tons per year. Ten tons is not that high in industrial level, but at the time, the production volume of single-walled CNTs in the world was estimated to be 6 tons.[9] If there was one super-growth synthesis furnace, it would be possible to manufacture more single-walled CNTs than the rest of the world. I thought this would be a breakthrough in terms of production volume and price.

If the super-growth method had 1,000 times the growth efficiency of the conventional method, the sales cost of single-walled CNTs that was several tens of thousands of yen per gram would become 1/1,000, or the sale price would be several tens of thousands of yen per kilogram. This would enable the use of single-walled CNTs as industrial material. I was certain that this would generate major innovation. This was the research topic that fulfilled my research policy.

3 Objective of the research

3.1 Development of mass production technology for single-walled CNTs

3.1.1 Industrial mass production method and technical concept

How do we realize industrial mass production based on the super-growth method?

When the article was published in *Science*, the sample size was about 1 cm square, the catalyst was formed by an expensive sputtering method, the substrate was a silicon wafer, and the synthesis was done one batch at a time. Industrial mass production was far away in the distance.

However, the super-growth method had several important characteristics in realizing the industrial mass production process, and we did not mention any of them in the *Science* paper. First, the super-growth method had the world's best synthesis yield of single-walled CNTs per volume and time of a reaction furnace. This meant that if we achieved mass production, we would be superior in terms of productivity and cost against other competing methods. Second, since super-growth involved adding water to the synthesis atmosphere of regular CNTs, we believed the process was scalable. Third, the super-growth method is a reaction process under atmospheric pressure without using vacuum, plasma, or high pressure. Due to these characteristics, we could construct an open system synthesis furnace. This was a great advantage in continuous synthesis. Finally, the optimal growth temperature of the super-growth method was 800 °C. This indicated that a metal synthesis furnace could be used instead of quartz or ceramic. From these characteristics, we imagined a manufacturing process for continuous synthesis of single-walled CNTs using a large metal synthesis furnace in an open system.

Figure 6 shows the process that we conceived as the mass production process of the super-growth method for single-walled CNTs at low cost while maximizing these characteristics. This was a process in which a metal film is used as substrate material, a catalyst is coated onto the film, continuous synthesis is done on a belt conveyor, and the substrate material can be reused.

What I find interesting is that the lab-scale synthesis process shown in the top part of Fig. 6 and the industrial mass production process shown in the bottom part of Fig. 6 are both super-growth methods, but the elemental technologies are totally different. The top is an academic process while the bottom is an industrial process. I think this figure clearly points out the large difference between academia and industry, and the difficulty of transferring technology developed in the academia to industry.

The manufacturing process where single-walled CNTs are continuously synthesized on flat substrate material was research that no one had ever attempted in the history of mankind, and it was necessary to conduct enormous amount of technological development. We expected it would kick off innovative effects, and we could build a network of intellectual properties that prevented entry of third parties. The innovative effect was the cost reduction to 1/1000 of the conventional method. However, there were many technologies that had to be developed and we could not fail in any area. If we failed in developing just one elemental technology, mass production would not be possible even if we achieved everything else. Therefore, it was obvious that this technological development would be extremely high risk and high return. Also, we could not utilize the existing manufacturing facilities for commercial production. Large facility investment was necessary for product realization.

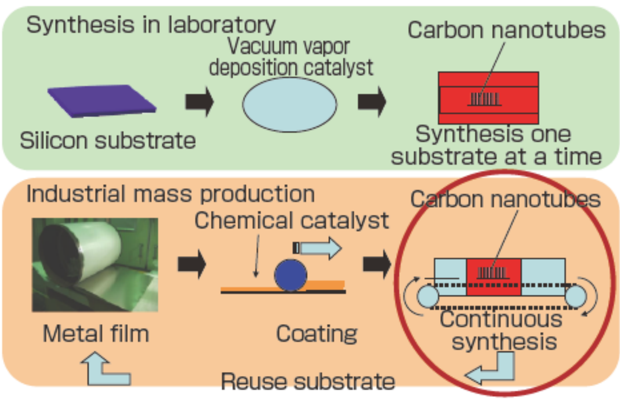

Fig. 6 Lab-scale vs. mass production process

There were mountains of difficulties and issues in realizing the mass production of single-walled CNTs by the super-growth method, but I was looking only at the possibilities of the super-growth method, not the difficulties.

3.1.2 Development of mass production technology in the NEDO "Carbon Nanotube Capacitor Development Project"

Fortunately, AIST obtained an opportunity to develop a mass production process by the super-growth method jointly with Zeon Corporation, in the "Carbon Nanotube Capacitor Development Project (FY 2000~2010)," a nanotechnology program of the New Energy and Industrial Technology Development Organization (NEDO) from 2006 (Fig. 7). It is presently known as a prime example of a successful national project, but it was fraught with hardship in the beginning.

First, one of the absolute conditions in starting the project was to find a partner company with whom we would develop the mass production technology by the super-growth method. Mr. Motoo Yumura who was my superior at the time contacted eight companies that were engaging in CNT R&D and interviewed some of the companies. All companies said, "The super-growth method is wonderful. But we have been conducting R&D for CNTs using our original technology. It is difficult to abandon this technology and switch over to the super-growth method." We were unable to meet a partner that would truly work on the mass production process by the super-growth method. Through an introduction, we met Mr. Kohei Arakawa who was the managing director of the Zeon Corporation.

Mr. Arakawa had experience in CNT research (at the time, it was called simply carbon, not CNT) when he was working at Nikkiso Co., Ltd. He listened to our story with zeal and keenness. He immediately calculated the cost of mass production, determined that it would be viable as business,

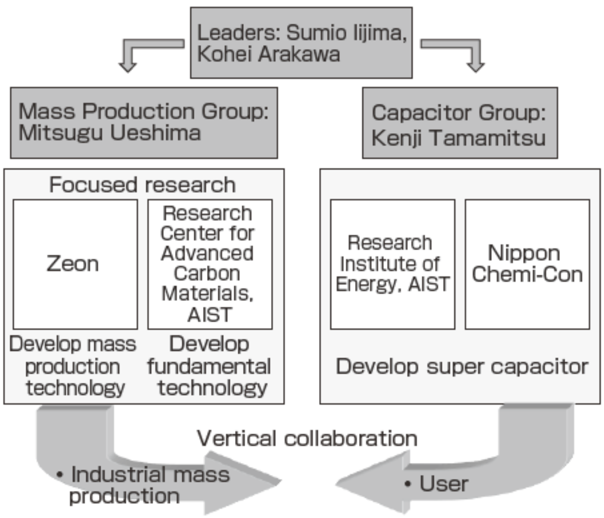

Fig. 7 Organization of Carbon Nanotube Capacitor Project

and obtained permission from the president to go forward on the R&D. I intuitively felt that super-growth would not be realized unless we teamed up with Mr. Arakawa.

Immediately afterward, the asbestos issue arose. In June 2005, it was reported that workers and families of two companies that were manufacturing asbestos died of malignant mesothelioma. Since CNT had a similar form as asbestos, there was concern that it might cause a similar health problem, and we were flooded with inquiries every day. The permission of CNT R&D was withdrawn, and it seemed we could no longer work with Mr. Arakawa. However, we did not give up. First, Mr. Arakawa asked us to evaluate the amount of CNTs that adhered to the HEPA filter in the laboratory. As a result, it was found that the concentration of CNTs floating in the air in the lab environment was lower than the concentration of asbestos in regular air. Mr. Arakawa directly requested the president for CNT R&D one day before the deadline for application to the NEDO Project, and obtained the president's permission for R&D.

While it felt like treading on thin ice, we were able to start the project with wonderful members who worked hard to realize the single-walled CNTs by the super-growth method.

4 Research scenario for achieving the goal

When the project started, we extracted the technical issues that had to be tackled. The main technical issues listed were as follows: the development of a substrate that was low cost and could be easily upscaled to a large surface area, to replace the silicon wafer; the development of a coating type catalyst to replace the iron thin film catalyst formed by the sputtering method; the development of synthesis technology for synthesizing uniform, vertical arrays by controlling and adding water to a large surface area at PPM level; the development of continuous synthesis technology to continuously transport the substrate material; and others (Fig. 8). Diverse technical issues also included the development of a metal synthesis furnace to replace the quartz furnace, cleaning technology of the furnace, reuse technology of the substrate material, generation of a low-cost gas atmosphere, and others.

Since it was necessary to solve all the issues in five years, we took an approach that we named the "black box strategy." First, we weighed all issues. The issues with absolutely no solution were labeled "black," the issues that could be solved with abundant human and monetary resources were "grey," and the issues that had been solved were "white." Next, the limited research resources were prioritized to turn the black issues grey. Also, to complete the whole picture in a short time, individual elemental technologies were developed concurrently as much as possible, and the elemental technologies were integrated later to complete the mass production process. For the roles of AIST and Zeon, AIST developed methods for solving the issues, and Zeon developed ways to upscale the methods, continuous synthesis, and production technologies.

The greatest black issue was "how to realize continuous synthesis." When we succeeded in continuous synthesis and this issue became grey, Mr. Arakawa would embark on building the commercial plant. At this point, the mass production process was not established at all. I thought Mr. Arakawa was the embodiment of an excellent business manager. Unfortunately, the bankruptcy of Lehman Brothers occurred and it became extremely difficult for the company to make facility investment, and the commercial plant ceased to be.

I shall explain the main elemental technologies including the development of substrate material, a coating type catalyst, large-area synthesis technology, and continuous synthesis technology. Then, I shall describe the course of the research where the elemental technologies were integrated to complete the mass production process.

4.1 Elemental technologies of the mass production process

4.1.1 Technological development of the substrate material

The production process at the time when the article was published in *Science* used a silicon wafer as the substrate, but for mass production, it was necessary to have a substrate that was low cost as much possible, was capable of synthesizing excellent quality single-walled CNTs at high efficiency, and could be reused repeatedly. Such a substrate must show high durability at synthesis temperature of nearly 800 °C, be highly resistant to hydrogen reduction and oxidation atmospheres due to water addition, and must not inhibit CNT synthesis. As a result of searching for a substrate that fulfilled such strict demands, it was found that single-walled CNTs could be synthesized at similar growth efficiency and quality as silicon wafers when a Ni-Fe-Cr alloy was used as substrate material.[10] Among dozens of materials investigated, only the Ni-Fe-Cr alloy satisfied all the necessary requirements (Fig. 9). We were lucky because the Ni-Fe-Cr alloy was also excellent from the perspective of continuous production and safety. The Ni-Fe-Cr alloy is called stainless or Inconel®, and it is the most widely used economic thermal resistant metal. In fact, the material of metal muffle furnaces used at temperature of 800 °C is usually Inconel®.

There was the problem of carburization, that is, metal was carbonized and weakened when exposed to carbon at high temperature. The raw material of CNTs is hydrocarbon. Moreover, the CNTs are synthesized at high volume continuously in the synthesis furnace, and that inevitably creates a highly concentrated hydrocarbon atmosphere. The effect of carburization was extremely powerful in such synthesizing atmosphere, and for example, the metal screw that joined the metal parts of the sample holder expanded due to carburization after several hundred syntheses and destroyed the sample holder. The Ni-Fe-Cr alloy was least affected by carburization or had a high carburizing resistant property.

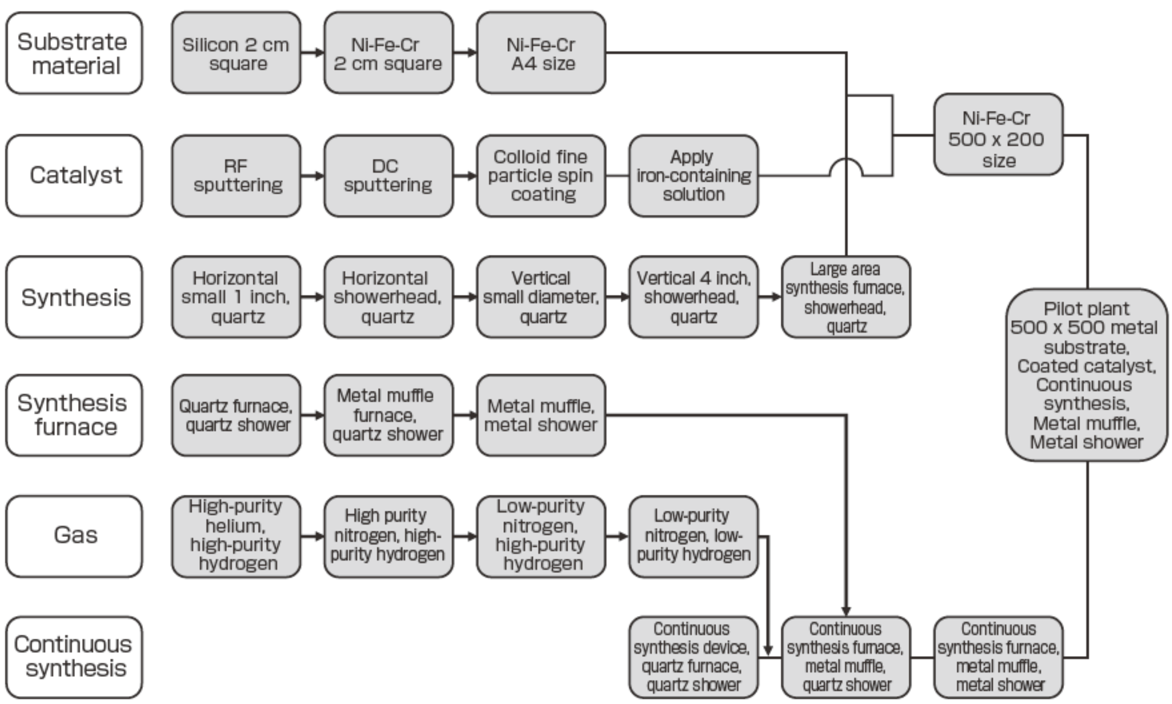

Fig. 8 Development of mass production technology

The excellent thermal resistance and carburizing resistant properties of the Ni-Fe-Cr alloy enabled the reuse of substrate material. Regular metals underwent plastic strain and deformation when they were repeatedly exposed to a highly concentrated hydrocarbon atmosphere at 800 °C and then cooled to room temperature, but these were minimal in the Ni-Fe-Cr alloy. This was one of the extremely important points in establishing the industrial mass production method by the super-growth method.

4.1.2 Technological development of the catalyst

In order to achieve high-speed synthesis of single-walled CNTs that are vertically aligned on the substrate material using the super-growth method, it is necessary for the catalyst to meet strict conditions. In later research, it was clarified that for the single-walled CNTs to grow vertically at millimeter-scale height, there was a sweet spot for the size and spacing of the catalyst[11] (Fig. 10). The sweet spot exists because the region is surrounded by multiple boundaries. That is, multi-walled CNTs are synthesized from large catalysts (multi-walled CNT boundary), while the growth rate of single-walled CNTs that grow from small catalysts are slow (low yield boundary), and CNTs grow laterally from the catalyst with large spacing. The typical catalyst size of the sweet spot is 3 nm, and the catalyst spacing is 15 nm. This catalyst array has to be stably present for at least 10 min in the synthesis temperature of 800 °C. To the present, the capable catalyst system is only obtainable when the iron thin film on the alumina catalyst support is subject to hydrogen reduction at high temperature of 800 °C.

The control factor that was crucial to place the catalyst in the sweet spot was the thickness of the alumina catalyst support and the iron catalyst, particularly the thickness of the iron catalyst. As a result of research, a single-walled CNT array could be synthesized only when the thickness of the iron catalyst was between 0.8 nm to 1.3 nm.[12] Therefore, the catalyst film was initially formed using the sputtering method that had excellent control of film thickness.

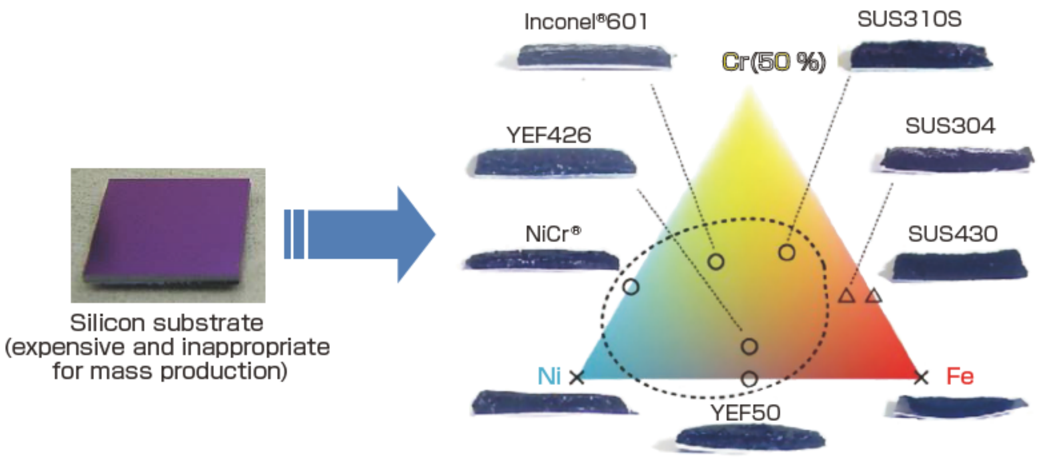

Fig. 9 Development of metal substrate

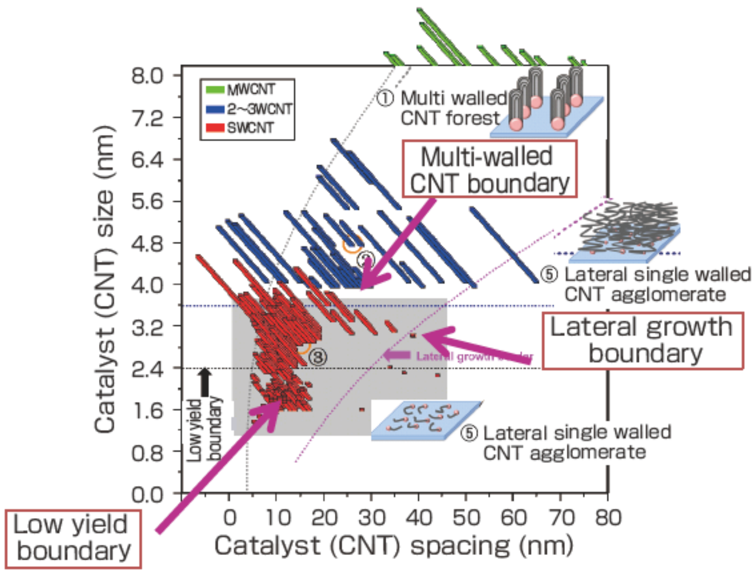

Fig. 10 Sweet spot for catalysts[11]

However, from the perspective of industrial mass production, the sputtering method had low productivity and high facility costs, and that meant high overall costs. Therefore, it was necessary to shift to wet catalysts that were low cost, needed small facility investment, and had high productivity. In the sputtering process when the article was published in *Science*, the iron catalyst was sputtered immediately after sputtering the alumina catalyst support with RF. However the RF sputtering of alumina had extremely slow film forming rate, and the productivity of the catalyst was significantly low. Therefore, we developed the technology in which the aluminum was DC sputtered in an atmosphere containing oxygen thereby oxidizing the aluminum on the spot to form the alumina. Through the series of research on catalyst development using sputtering, it was found that various factors such as the composition of alumina catalyst support and surface smoothness greatly affected the growth of single-walled CNTs.

Thinking that the thickness restriction for the iron catalyst was too strict and that it was difficult to apply the iron thin film evenly within the allowed range, we developed iron colloid nanoparticles as wet catalysts synthesized in the iron carboxyl solution (Fig. 11).[13] By thinly coating the iron colloid nanoparticles onto the silicon substrate using spin coating, we were able to grow single-walled CNTs similar to the ones by sputtering thin films. However, when it was investigated closely, the single-walled CNTs did not grow from individual iron colloid nanoparticles. It was found that the iron colloid nanoparticles fused when the catalyst was reduced by hydrogen before synthesis, and then turned back into fine particles again. Therefore, when wet catalysts were used, application of a thin coat to the iron catalyst film was also sufficient.

We first looked at the method called capillary coating as a method of coating the ultra-thin iron film. This was a method for coating the substrate material with a solution containing iron salt that was sucked into the ultra-fine tubes by the capillary effect, and then used for evenly coating substances

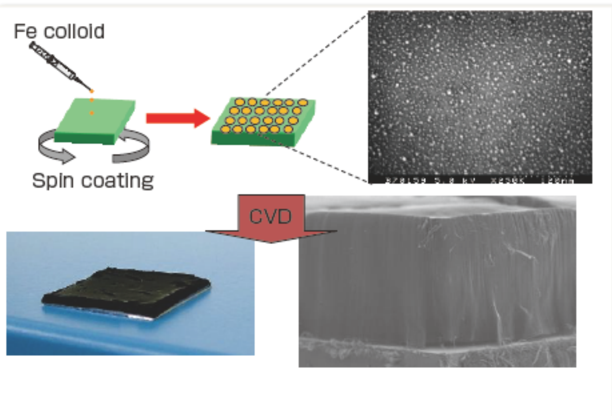

Fig. 11 Development of coated wet catalyst[13]

such as liquid crystals. Using this method, we succeeded in coating ultra-thin iron catalysts onto a flat substrate material, but due to its principle, we were unable to apply the solution evenly to a substrate with distortion or deformation. From the experiments for large-area synthesis, we found that the distortion and deformation of substrates increased as the substrate material increased in surface area and as the substrate material was reused repeatedly. Therefore, we were forced to develop a totally different method. After many twists and turns, we finally succeeded in coating the ultra-thin iron film onto large-area deformed substrate material by the wet method, and this was a very inexpensive and highly productive method for growing single-walled CNTs.

Next, like the iron catalyst, we conducted technological development for coating with alumina catalyst supports. Since alumina had extremely high carburizing resistant property, the substrate material consisting of Ni-Fe-Cr alloys coated with alumina catalyst supports showed excellent durability in the highly concentrated hydrocarbon environment used in the super-growth method. The catalyst we developed became a system that powerfully inhibited the deformation and carburization that were problems in reusing the large-area substrate material.

4.1.3 Development of the synthesis technology optimal for mass production

It was necessary to conduct much technological development for the mass production process in synthesis technology. When the article was published in *Science*, the CNT was synthesized by placing the substrate horizontally in a horizontal synthesis furnace of 1 inch diameter and supplying ethylene and water vapor gas from the side. This small, horizontal synthesis furnace had an optimal structure for creating a laminar flow and preventing gas turbulence. Any gas turbulence significantly decreased the synthesis efficiency of CNTs, and such equipment configuration was optimal in lab scale synthesis. However, this lab scale synthesis furnace or substrate material could not be upscaled to an industrial scale. There was a major problem that most of the supplied gas did not hit the substrate, passed over the catalyst without reaction, and only about 1 % of the supplied ethylene gas was converted to CNTs.

It was necessary to supply the gas from the top to enable upscaling of the synthesis furnace and substrate material, and to greatly improve the conversion rate of the carbon source to CNTs. Therefore, we developed a showerhead (Fig. 12).[14] Various changes were made to the showerhead to evenly supply extremely minute amount of water to the catalysts on the substrate material. Next, the synthesis furnace was made vertical and the diameter was increased from 1 inch, to 2 inches, and then 4 inches. When the furnace was turned vertical and the diameter increased, turbulence occurred immediately. We conducted fluid simulation and created several prototypes of the gas supply system and the showerhead that allowed even supply of trace water to the substrate material without turbulence.

4.1.4 Technological development of the scalable metal synthesis furnace

The development of the synthesis furnace itself was a major element in technological development. At the time of publication in *Science*, we used a quartz furnace. There was a size limitation to a manufacturable quartz furnace, and it was expensive. It was necessary to make a metal furnace. However, in continuous synthesis, the furnace would be exposed continuously to high temperature and highly concentrated hydrocarbon. The specs required for the synthesis furnace were more severe than those for the substrate material.

Therefore, a dedicated device was introduced to study the materials that were resistant to the synthesis atmosphere with long-term stability. Using this device, deterioration, carbon adhesion, and carburization of the materials were investigated by exposing several candidate materials for a long time to high temperature and to highly concentrated hydrocarbon. The carbon gases and the reaction of trace water and metals greatly affect the synthesis. The material of the furnace was selected considering the effect on CNT synthesis and the long-term durability in the synthesis environment, and the selected materials were used in the actual small synthesis furnace. The metal showerhead was developed after the synthesis furnace, and we finally succeeded in developing a synthesis furnace that did not use quartz.

When the synthesis of CNTs was repeated many times, carbon impurities built up in the synthesis furnace. These carbon impurities had major effects on CNT synthesis by absorbing the water added to the synthesis atmosphere. The furnace had to be cleaned after a certain amount of impurities adhered. Carbon that adhered under high temperature was crystallized and removal was difficult. The easiest method was combustion by introducing oxygen at high temperature, but if that was done, the metal furnace would be damaged by oxidation and its lifespan would decrease. Therefore, we developed a cleaning technology to remove the carbon impurities without damaging the metal synthesis furnace.

4.1.5 Large-area synthesis technology

The technologies were taken further to develop a large-area synthesis furnace that could synthesize on large-area substrate material (A4 size or more) (Fig. 13). When the furnace was upscaled by a batch method, about one hour or more was necessary to heat the furnace to synthesis temperature. However, in continuous synthesis, it was necessary to raise the temperature of the substrate material to synthesis temperature in about 10 min. To alleviate this difference, we developed an extremely special large-area synthesis furnace. In this synthesis device, the large-area substrate material was stored inside the quartz horizontal furnace of 300 φ, and the gas was replaced. A large muffle furnace was placed next to it, and this was maintained at synthesis temperature. The high-temperature muffle furnace moved on rails to envelope the quartz furnace to quickly raise the temperature and heat the substrate material. This format was employed to conduct large-area synthesis at thermal history close to the future continuous synthesis as much as possible. After such technological development, we succeeded in large-area synthesis of A4 size and A3 size.

4.1.6 Continuous synthesis technology

The final, most crucial technological development was the development of continuous synthesis technology. Several continuous syntheses and quasi-continuous methods were considered, and finally, a method in which large substrate material was placed on a belt conveyor and transported continuously to the synthesis furnace was employed (Fig. 14). The characteristic of this method was that there were no shutters or partitions on the synthesis furnace, and it was designed as a complete open system. The substrate that entered the continuous synthesis furnace was transported to different areas. First, it was heated in the heating section,

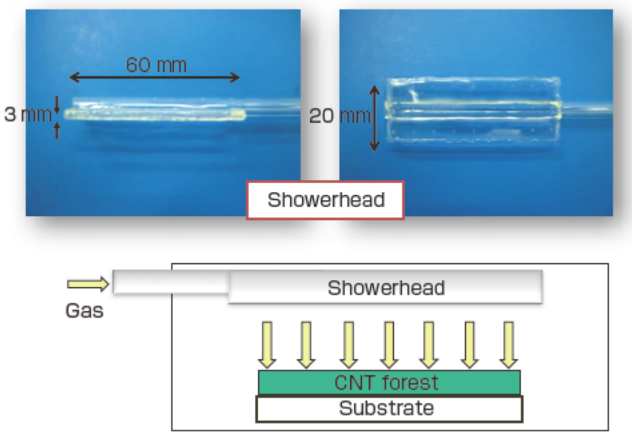

Fig. 12 Development of the showerhead[14]

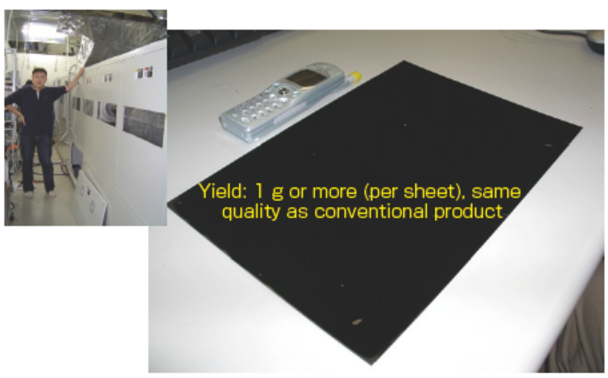

Fig. 13 Technological development of large-area synthesis

exposed to hydrogen atmosphere in the catalyst formation section, and the iron film was reduced to fine catalyst particles. The CNTs were synthesized in the synthesis section, and the temperature of the substrate material was decreased in the cooling section. The substrate material transported on the belt conveyor in the synthesis furnace underwent several processes continuously. To realize this in the synthesis furnace without shutters or partitions, gas showers were set between each section, to establish sections where the gases were separated although they were connected spatially. The continuous synthesis furnace introduced showed growth of CNTs from the very first substrate, and I was thoroughly impressed by the engineering capability of the company.

4.1.7 Integration of the elemental technologies

While developing the elemental technologies such as substrate material, a catalyst, large-area synthesis technology, and continuous synthesis technology, these technologies were integrated at the same time. Ultimately, unless all elemental technologies were integrated, we would not have a mass production process. However, when the elemental technologies were integrated, the complexity of the technology increased and new technical issues arose.

For example, silicon substrate material was used at first, and the technological development was conducted to replace it with a metal substrate. The size considered was 2 cm square. Several substrate materials were tried to see which 2 cm square was optimal for CNT synthesis. As a result, it was found that Inconel® was optimal. However, since Inconel® contained high amount of nickel, the nickel content had to be reduced to a minimum to reduce the cost. Next, the metal was upscaled to A4 size and growth took place in the large-area synthesis furnace. It was then found that heat distortion occurred when thermal history was added to the large-area metal substrate material, although this was not a problem in small size material. Of course, thermal distortion could be prevented if thicker substrate material was used, but this became costly. Also, the added weight of large-area material made the handling more difficult. Moreover, time was required for heating and cooling, and it could not be used in the continuous synthesis furnace. Therefore, we had to seek a solution that simultaneously fulfilled these conflicting factors.

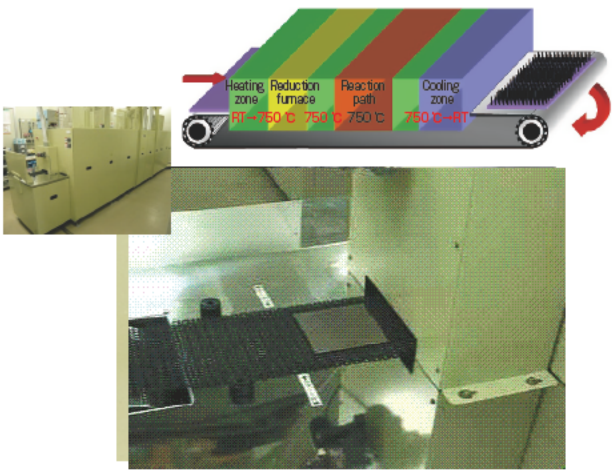

Fig. 14 Technological development of continuous synthesis

The integration of technology continued. In fact, sputtered catalysts were used in all the research described above. Therefore, we shifted to wet catalysts and the same considerations were repeated. The density and evenness of the wet catalysts were inferior to the sputtered catalysts, and thermal distortion occurred. When thermal distortion occurred in large-area substrate material, the coating with catalysts became difficult.

Next, we had to reuse the substrate material. It had to be reusable many times or else the cost of the substrate would be added to the cost of the final product. However, if the substrate material was reused, the material would have double, triple, and quadruple thermal history, thermal distortion would accumulate and increase, and it would become more difficult to fulfill all other technological elements at the same time. We had to strike a balance among such diverse factors, and at the same time develop technology to inhibit the negative factors such as thermal distortion. Each elemental technology was integrated to complete the mass production process.

5 Current status of the research and its future

5.1 Commercialization by Zeon Corporation and future prospect

When we succeeded in continuous synthesis, Mr. Arakawa started to consider practical use. In terms of the "black box strategy," we had no more technical issues that could not be solved, and the mass production technology would be completed if sufficient money and manpower were invested. However, the bankruptcy of Lehman Brothers occurred, and the economic situation turned difficult for companies to invest in facilities, and the move toward realization stopped. At that time, the director of METI came for a visit, and advised us to go for product realization using the supplementary budget.

Through such course of events, the pilot plant was built on AIST grounds using the facility funds of the supplementary budget. This plant was managed jointly by AIST and Zeon. The pilot plant was 12 m in length, the muffle furnace was an open system on both ends, the gas sections were created using multiple gas showers, and the super-growth single-walled CNTs were manufactured continuously on a substrate of 50 cm square transported on a belt conveyor.

It was designed by integrating the technologies nurtured in the development of continuous synthesis technology and large-area synthesis technology. Other than the continuous synthesis furnace, the continuous sputtering device, wet catalyst coating device, CNT harvesting device, substrate washing device, and others were added. The mass production process developed in the “Carbon Nanotube Capacitor Development Project” was realized, though at a small scale, and this enabled manufacture of super-growth single-walled CNTs at production volume of 100 gram/hour.

The manufactured super-growth single-walled CNTs were supplied to a wide range of domestic companies as sample supplies from AIST. Over 200 agreements have been signed to the present.

From FY 2013, the pilot plant was loaned to Zeon, and the super-growth single-walled CNTs were sold by Zeon utilizing the Result Diffusion Project. We approached the B2B format one step at a time.

Many prospective uses were developed from the super-growth single-walled CNTs that were supplied throughout Japan from the pilot plant, and this spurred actual realization. In the Technology Research Association for Single Wall Carbon Nanotubes (TASC), the technologies to utilize the super-growth single-walled CNTs were developed one after the other, including dispersion, coating, evaluation, forming, and compositing. This led to the development of various parts with excellent properties such as CNT rubber composite material with high thermal resistance, CNT carbon fiber rubber composite material with high heat conductivity, and CNT copper composite material that can pass 100 times the electric current while possessing the same electro-conductivity as copper,[15] and thus the development by companies was accelerated.

The market demand for super-growth single-walled CNTs, development of peripheral technologies such as dispersion and composition, and development of marketable application moved Zeon Corporation to start operation of a commercial plant in 2014. The ceremony for the start of the plant construction was held in Tokuyama in November 2015. I was able to snap a photograph in front of the plant with Dr. Sumio Iijima (former Director, Nanotube Research Center, AIST), Dr. Yumura, Mr. Arakawa, Dr. Mitsugu Ueshima (Zeon), and Dr. Norimitsu Murayama (Director, Department of Materials and Chemistry, AIST) (Fig. 15), and this was when I felt we reached a milestone. Plant construction and the commercial production of super-growth single-walled CNTs are only the starting line in the business world. To grow this business, there are mountains of difficulties and issues that must be overcome. However, since the super-growth single-walled CNTs have overwhelming superiority in purity, length, and specific surface area compared to other CNTs, I believe it will become a major business.

Finally, I believe that it is possible to see the prospect of CNTs in the future by looking at the periodic table of elements. Carbon is the sixth element in the periodic table. The first and second elements, hydrogen and helium, are gas, third element, lithium, is water prohibitive, and fourth, beryllium, is highly toxic. Carbon is the topmost element of the periodic table that can be used safely by humankind in a solid state. This means that carbon has a small nucleus and therefore is the lightest and has the strongest shared bond. CNTs that combine carbon in ideal structures are materials that can bring out the performance of carbon to the maximum. The periodic table tells us that we cannot create any material that is stronger or lighter than CNTs on the earth. If CNTs are fully commercialized, I believe that they will continue to be used as long as human society exists.

CNTs that were found in Japan will grow into a CNT industry that originated in Japan. They will be used in all corners of society making it a place where “carbon nanotubes are here, there, and everywhere,” and will benefit human society. My goal is to create such a future.

6 Acknowledgements

I am sincerely thankful to Sumio Iijima, Don Futaba, Shunsuke Sakurai, Satoshi Yasuda, Akiyoshi Shibuya, Hirokazu Takai, Mitsugu Ueshima, Kohei Arakawa, Mitsuhito Hiroda, and Motoo Yumura with whom we advanced this research.

This paper is based on the results obtained in the “Carbon Nanotube Capacitor Development Project,” a program of the New Energy and Industrial Technology Development Organization (NEDO).

Fig. 15 Photograph in front of the carbon nanotube manufacturing plant (Tokuyama Plant, Zeon Corporation)

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Author

Kenji HATA

Graduated from the Department of Applied Physics, School of Engineering, the University of Tokyo in 1996. Joined AIST in 2003. Currently, Director, CNT-Application Research Center, AIST. For the development of mass production technology for single-walled carbon nanotubes by super-growth method, received: the 21st Century Invention Encouragement Award, 2016 National Invention Award (Japan Institute of Invention and Innovation); Commendation for Science and Technology (Development) by the Minister of Education, Culture, Sports, Science and Technology; and Special Jury's Prize of the 45th Japan Industry and Technology Prize (Nikkan Kogyo Shimbun).

Discussions with Reviewers

1 Overall

Comment (Toshimi Shimizu, AIST)

This paper presents the course of research in which the innovative synthesis method for single-walled carbon nanotubes developed by the author was advanced from laboratory scale to industrial mass production scale, and the commencement of operation of the world's first mass production plant by a company. The diverse elemental technologies that were determined essential according to the research policy conceived by the author and the scenario for the integration of elemental technologies through corporate collaboration are briefly summarized. The passion of the author and the company propelled the realization of the manufacturing process design for nanomaterials for which there was very little previous experience, and this is world-class nanotechnology that is certainly appropriate for publication in *Synthesiology*.

Comment (Shuji Abe, Musashino University)

This paper offers a clear overview of the development of production technology for single-walled CNTs by the super-growth method developed by the author, from the motivation of development, the efforts spent on the project, the elemental technologies for a mass production process, and the current commercial production. In the first draft, there were many places where the author's "strong thoughts" were presented in literary expression like in a memoire or an essay. While these make the paper very unique, they can also make the paper awkward as an academic article. *Synthesiology* is, in principle, a public academic journal, and the editorial policy is "to publish papers that explain the research process and the results aiming for the introduction of research results into society in the words of science and technology." Overall, this paper is written in the words of science and technology, and although I think some literary expressions are permissible, I also feel that they should not be excessive.

2 Comparison of the methods for single-walled CNT synthesis

Comment & Question (Toshimi Shimizu)

The author cites Fig. 3 to compare the yield, cost, purity, and quality of the various methods of single-walled CNT synthesis. On the other hand, the paper discusses the superiority of the super-growth method against other innovative synthesis methods for single-walled CNTs, from the perspectives of synthesis yield per volume and time of the reaction furnace, reaction environment (vacuum system, open system, etc.), and reaction temperature. In Fig. 3, for example, if you weigh each score like excellent 4 points, good 3, moderate 2, and poor 1, the supported catalyst CVD method and fluid bed furnace method have a total of 10 points, while the super-growth method has 11 points, and there is not much difference. I think the general readers will intuitively understand the superiority of the super-growth method if you add, as items of comparison, the three items discussed in this paper: synthesis yield, reaction environment, and reaction temperature. Or, is the author's weighing of the scores for the four items of comparison in Fig. 3 different from each point mentioned above?

Answer (Kenji Hata)

The four items shown in Fig. 3 show the characteristics of carbon nanotubes, and they show that the super-growth method is viable as business compared to the conventional synthesis methods. As you indicated, items such as synthesis yield per volume and time of the reaction furnace, reaction environment (vacuum system, open system, etc.), and reaction temperature are discussions about the synthesis condition. Since there are diverse synthesizing formats for each synthesis method, it is difficult to discuss the superiority or inferiority in simple terms. Also, considering practical application, I don't think it is very meaningful to score the items of Fig. 3 as poor 1 point, moderate 2, good 3, and excellent 4.

3 Safety of the single-walled CNTs

Comment (Toshimi Shimizu)

In the first draft, there was an expression that the researchers involved in development might quietly disregard the matter of safety of the single-walled CNTs. For the safety of single-walled CNTs, as a result of the NEDO Project, the safety test manual and guidelines for the work environment and measurements for carbon nanotubes have been published for the workers who handle the CNT materials. I recommend that you add or cite appropriate explanations and results of the concurrent R&D for the ELSI (ethical, legal, and social issues) and EHS (environmental, health, and safety) concerns that are essential in the development of nanomaterials.

Answer (Kenji Hata)

I corrected the text so the explanation centers on the activities conducted primarily by AIST and Zeon. At the time, the NEDO Project that led to the drafting of the safety test manual and work environment guidelines for carbon nanotubes manufactured by the super-growth method had not been implemented. Since this departs from the main topic of this paper, I did not discuss the details of the various kinds of EHS research that were conducted concurrently.

Comment (Shuji Abe)

In the first draft, though it may not be representative of the author's thinking, there was a text that the readers might mistake that you are scientifically negating the health damage of asbestos. I recommend you correct the text appropriately.

Answer (Kenji Hata)

As you indicated, I corrected the expression that may give the readers the impression that I am negating the health effect of asbestos that has been scientifically proven.

4 Mass production of single-walled CNTs

Question (Shuji Abe)

What specific degree of production volume do you mean when you say "mass production" in "3.1 Development of mass production technology for single-walled CNTs"? There was a description in Subchapter 2.2, that you set a personal goal of "10 tons annually," but can I assume that the Zeon's CNT production plant that started operation in 2015 surpassed this goal?

Answer (Kenji Hata)

Zeon has not released the actual figures. Therefore, I shall not publish the figures in this paper.

5 Grade and quality assurance of single-walled CNTs

Question (Toshimi Shimizu)

In the case of multi-walled CNTs, I think the diameter, length, purity, metal oxide amount, specific surface area, and others are noted as their qualities. What are the parameters to assign the grade and to assure quality of the single-walled CNTs that were massively produced here? Do you conduct the quality control by using Raman spectroscopy, optical absorption spectroscopy, or thermogravimetry?

Answer (Kenji Hata)

In general, the carbon nanotubes synthesized by the super-growth method have the characteristics of high specific surface area, high purity, and long length, and actual quality control is done based mainly on purity and specific surface area.

6 Elemental technologies of the mass production process

Comment (Toshimi Shimizu)

You present the division of roles where AIST develops the method for solving the issues, and Zeon Corporation develops the ways to upscale the methods, continuous technology, and production technology. In "4.1 Elemental technologies of the mass production process", can you color-categorize each elemental technology (currently grey) in Fig. 8 into those achieved by AIST, Zeon Corporation, or AIST + Zeon Corporation. In this paper, there are no names of the people in charge of the development of individual elemental technologies described in Subchapter 4.1. I think the reader's understanding will deepen if people or organizations in charge are clarified.

Answer (Kenji Hata)

Since this paper was written by AIST alone, I described the parts in which AIST was primarily in charge. However, to help understanding of the whole flow, I explained the parts where Zeon was in charge as much as they were disclosed. For the division of research topics between AIST and Zeon, AIST developed the fundamental technology while Zeon developed the mass production method. The research for large-area synthesis and continuous synthesis was mainly conducted by Zeon.

Comment (Shuji Abe)

In "4.1 Elemental technologies of the mass production process," you describe the development of various elemental technologies, and I think you should discuss the contributions of teams and joint researchers for particularly important technologies. If it is difficult to mention them individually, it can be placed at the end in a form of acknowledgement.

Answer (Kenji Hata)

Since it is difficult to mention them individually, I added the acknowledgement of the people involved.

7 Integration of the elemental technologies

Comment (Toshimi Shimizu)

The section of "4.1.7 Integration of the elemental technologies" is an overlap of the contents in 4.1.1 to 4.1.6. Here, why don't you give us the final summary of the results of integration and the conclusion of results as much as you are allowed to disclose. I think the readers can readily understand if you refer to Fig. 8.

Answer (Kenji Hata)

The integration of elemental technologies is what we spent most effort on, and there are many parts that cannot be disclosed at this point, and it is very difficult to comprehensively describe the whole picture. However, it was the part on which we spent most effort, and I decided to give some details using case studies. Please understand that this paper was written under such restrictions.