Carbon Nanotubes, Materials for Nanotechnology

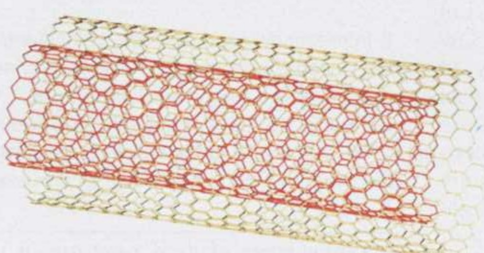
By Yumura Motoo

Introduction

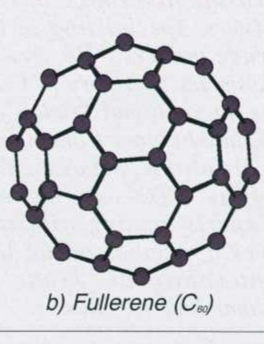
Nanotechnology is the technology by which we can utilize materials as elements in a world with a scale of 10^{-9}m. With nanotechnology, we can manipulate atoms and molecules at our will in the nano-scale world and develop products with new functions. It is highly expected that nanotechnology can be used to develop powerful tools to overcome the difficult economic situation. We can apply this technology to materials, information technology (IT) equipment and medical technologies. Japanese companies have accumulated technologies through the development of semiconductors and miniature machining. If we successfully develop nanotechnology, the restoration of the Japanese economy will be possible. Carbon nanotubes, which were discovered by a Japanese researcher, have drawn significant attention as materials for nanotechnology.

Figure 1

Atomic model of a carbon nanotube and Fullerene (C_{60})



a) Carbon Nanotube

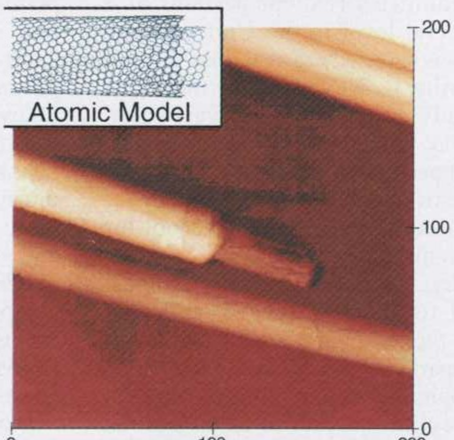


b) Fullerene (C_{60})

Carbon nanotubes (Figure 1a) were discovered by Dr. Iijima Sumio of NEC Corp. in 1991.[1] At the time when carbon nanotubes were discovered, they were not so popular among scientists, but most research focused on C_{60}.[a] (Figure 1b) Thereafter, however, scientists were surprised by the characteristics of this discovery. This is the world's strongest fiber that has been discovered so far; the conductivity of electricity is higher than that of copper and the conductivity of heat is higher than that of diamond. Moreover, it is resistant to extreme heat and is lighter than aluminum. It seems to us that mankind will not be able to develop a more excellent material than this one.

Figure 2

Scanning tunneling microscope image of multi-walled carbon nanotubes which were synthesized and purified at AIST



The fields of research for carbon nanotubes include production methods, analysis of the growth mechanism, the process for producing membranes, analysis of structures, analysis of various kinds of physical properties, and research and development (R&D) for application and theoretical analysis. They are developing so rapidly that we have no time to catch our breath. In this paper, we will introduce our R&D results concerning the industrial use of carbon nanotubes implemented at the Ministry of Economy, Trade and Industry (METI).

Synthetic Research Marked the Beginning of the Science of Carbon Nanotubes

The discovery of multi-walled carbon nanotubes by Dr. Iijima was the start of the science of carbon nanotubes. Carbon nanotubes were discovered as the by-product of C_{60} which was produced using carbon arc discharge apparatus, and after that many scientists focused on studying the measurement of the physical properties of carbon nanotubes.

Development of purification method for carbon nanotubes

It seems that the accomplishment of the isolation of C_{60} by the arc discharge method which has been materialized by Dr. Donald R. Huffman and other researchers brought about the remarkable development of C_{60} after 1991.

However, it was much more difficult to isolate carbon nanotubes because they are insoluble, while C_{60} is soluble.

We tried to apply the high temperature method for the extraction of multi-walled carbon nanotubes from the cathode deposit which was produced by carbon arc discharge apparatus. Though we tried this method using an even more effective solvent at a high temperature, we couldn't succeed. The isolation technique based on powder technology was then applied, and the separation and purification of multi-walled carbon nanotubes was achieved in a short period. We observed these purified multi-walled carbon nanotubes by scanning tunneling microscopy (STM) and succeeded in taking their clear STM image (Figure 2) for the first time in the world.[2] While studying the physical properties of purified multi-walled carbon nanotubes, we developed a more effective chemical method for their purification.[3] In this field also, we took the first step in the world.

Moreover, multi-walled carbon nanotubes themselves, purified by a chemical purification method, have a beautiful edge, and we noticed that they had excellent physical properties for electron emission.[4] (Figure 3) Thus, the possibility of a wide range of applications of carbon nanotubes has been discovered.

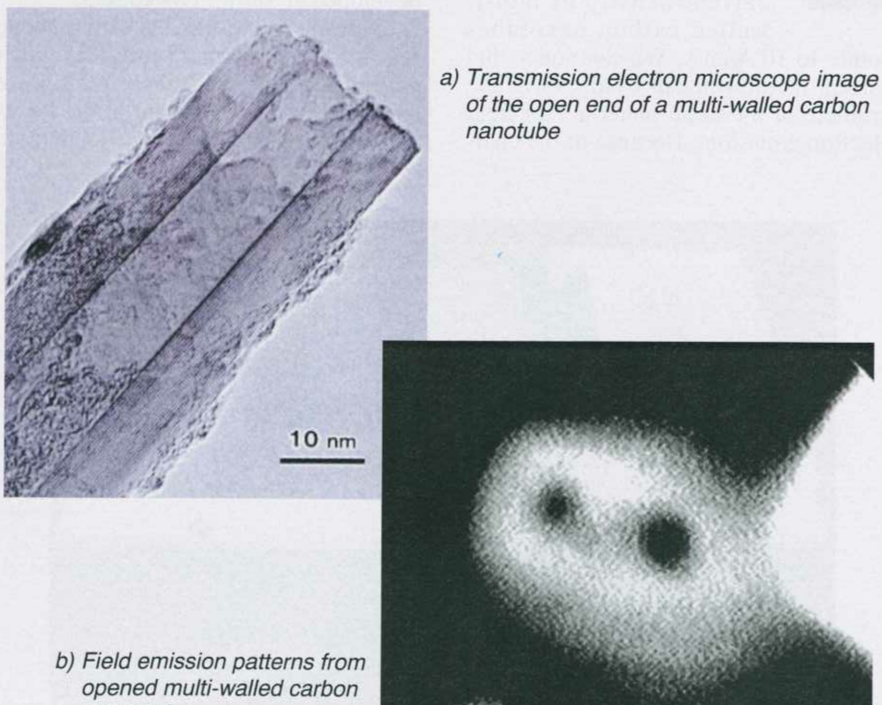
Industrialization of Carbon Nanotubes – Development of the Method for Mass Production and Application to Field Emission Display (FED)

Since the discovery of multi-walled carbon nanotubes by Dr. Iijima, several basic types of research have been carried out. After carbon nanotubes were recognized as a promising material for electron discharge, the circumstances of the research involving this material have changed – the amount of both basic and applied research is increasing and there is keen competition among these researchers.

Many characteristics of carbon nanotubes are gradually being discovered. We expect that these characteristics will apply to various fields. In order for Japanese industry to become more internationally competitive, we think that the urgent task is to push forward the development of products to which the various characteristics of carbon nanotubes are applied. To achieve this task, we have to develop the technology to produce several kilograms of carbon nanotubes a day. Therefore we immediately have to develop the chemical synthesis method using ultrafine particles as the catalyst which, we think, will make it possible for us to carry out industrial mass production.

Figure 3

Field emission from multi-walled carbon nanotubes (Y. Saito et al., *Nature*[3])



a) Transmission electron microscope image of the open end of a multi-walled carbon nanotube

b) Field emission patterns from opened multi-walled carbon nanotube

The development of the chemical synthesis method using ultrafine particles as the catalyst

In October 1998, the Frontier Carbon Technology (FCT) project was launched, and R&D for the technology of mass-production of carbon nanotubes has fully started with the participation of Showa Denko K.K.

It has already been recognized that multi-walled carbon nanotubes were produced as the vapor grown carbon fiber (VGCF)[6] by the growing method, and a patent application for this product was made in the 1980s. Japan was the first country to discover the VGCF. With this method, we obtained multi-walled carbon nanotubes by putting carbon gas into an electric furnace tube, and making it touch the catalytic metal fine particle.

The research has been developing smoothly, and in December 1998 we found important factors in the catalyst system and reaction system. With this result, we started to construct a pilot plant for the large-scale synthesis of multi-walled carbon nanotubes in the factory of Showa Denko K.K. in Kawasaki in March 1999, ahead of the planned construction date of 2000. This plant was completed in September, and we have already started operations there. In December we succeeded in producing the expected amount of 200g of multi-walled carbon nanotubes per hour. (Figure 4)

Figure 4: The pilot plant for the mass production of multi-walled carbon nanotubes

Photo: Showa Denko K.K.

Development of application of carbon nanotubes to FED

An electron source using carbon nanotubes has excellent properties – including the fact that no heat is necessary and that we can obtain a brighter electron beam – which is different from the usual heat electron emission style. Therefore, it is expected to become the next generation electron source of FED. In the joint research program with Dr. Saito Yahachi of Mie University, we measure the electric current density of the field electron emission from each carbon nanotube which have been purified by the method developed at the National Institute of Advanced Industrial Science and Technology (AIST). We noticed that the electric current density of carbon nanotubes was 10^8A/cm^2. This surprising electric current density is higher than the highest value measured for the usual electron emission material. This proves that carbon nanotubes are excellent material for electron emission.

Using these carbon nanotubes, Ise Electronics Corp. has successfully produced an experimental FED with the electron source coming from carbon nanotubes.

The panel size of the field emission display of the experimental product (Figure 5) is 120x100nm and the thickness of the panel is 10nm. Although this was not equipped with a vacuum pumping system (the inside vacuum rate is about 10^{-6} torr), this panel emitted light with sufficient brightness – the usual field emission electron source needs a high vacuum condition and vacuum pumping system.

This experimental product proved to be an excellent property of the field emission electron source using carbon nanotubes.

It is a fact that the electric current density of multi-walled carbon nanotubes comes to 10^8A/cm^2. We can notice that carbon nanotubes can easily solve the problem of the usual materials for field electron emission. Because of the characteristics of these tubes, researchers are impressed with the possibility of nanotubes as materials for electron emission, and the characteristics of carbon nanotubes have created a great sensation in Japan. The experimental field emission display has shown that carbon nanotubes are promising materials. We have also developed the technology to mass-produce carbon nanotubes, which enable us to supply them at a low price. Our work stated above has drawn a lot of attention both inside and outside Japan, and reversed the idea of the industrial world that new material has little practical use. Researchers have quickly become interested in carbon nanotubes.

Putting Carbon Nanotubes to Use as Industrial Materials

In the FCT project which started in 1998, the development of the technology for mass-production of carbon nanotubes has been carried forward step by step, integrating the technology of the catalyst developed at AIST and the technology for the large scale reactor developed at Showa Denko K.K.

Using the achievements of the above research, we began to provide multi-walled carbon nanotubes, which are produced in the pilot plant at the factory of Showa Denko K.K., to private

Photo: Ise Electronics Corp.

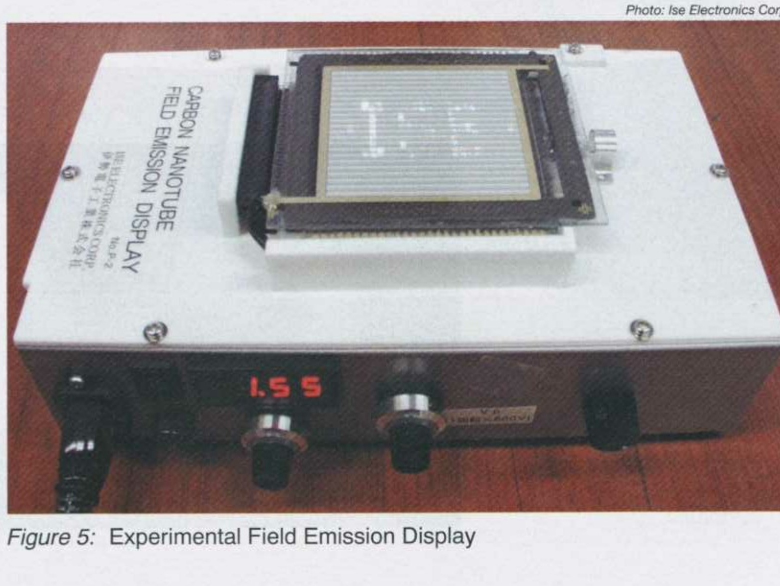
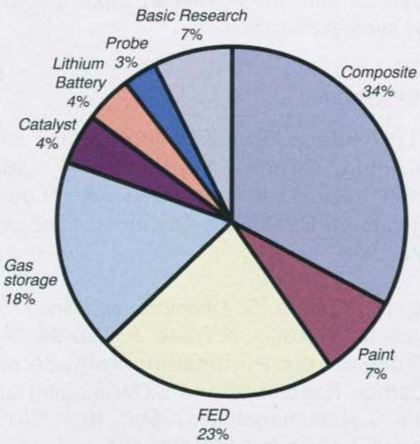


Figure 5: Experimental Field Emission Display

Figure 6

Putting carbon nanotubes to use as industrial materials –
Targets for the industrial utilization of carbon nanotubes
(Sample distribution project)



companies and universities in Japan. We also promote the application of multi-walled carbon nanotubes in Japanese industry.

More than 30 private companies in various fields from the electric industry to the chemical industry contributed to the development of this research. Multi-walled carbon nanotubes are recognized as promising material for electron emissions, and after the FCT project is finished, the development of FED using multi-walled carbon nanotubes as the cold electron source will be expected. Furthermore, we find that these nanotubes are excellent electrode materials for batteries and the storage materials for hydrogen which are important for equipment such as fuel cells and materials for batteries, and we are applying these tubes to composite materials such as ultrastrong fiber stand resin with high conductivity. (Figure 6)

Our aim of making the multi-walled carbon nanotubes mass-produced in this project widely available to companies and universities in Japan has been welcomed by the industrial sector, and people have changed their views about the national project.

Carbon Nanotubes – Materials for Nanotechnology

Our increasing attention to the recent development of nanotechnology has even expanded to influence the social and political arenas, but scientifically, nanotechnology has the potential power to form a new field, not limited to the two areas above, such as chemistry, solid physics, electric engineering and bio-chemistry. Nanotechnology will surely become one of the most important fields at the beginning of the 21st century.

Electronics based on the silicon semiconductor has made remarkable progress in the latter half of the 20th century because of the search for higher speeds and devices with more integrated circuits. We made a great effort to downsize electric devices in the integrated circuit (IC). The technology for micro-lithography has helped us to do this, and with this technology we can manufacture an IC silicon semiconductor with a size of 0.1mm. However, the smallest size of IC we think we can manufacture is 0.05mm. This size may be the limit that we can manufacture with the silicon semiconductor technology. If the downsizing limit for ICs is about this size, it is natural to say that we cannot make a computer which is about the size of a sugar cube. In order to resolve this difficult situation for making a computer of this size, the density of the IC needs to be about 100 billion/cm^2, which is 1000 times greater than that of the present IC.

The technology which generally helps the downsizing stated above is nanotechnology. The most important material for nanotechnology is not silicon, but the materials which have electric functions in themselves such as DNA. If we want to use nanotechnology we have to use parts with this size and function. Carbon nanotubes were discovered at the time when there is a potential demand for such technology.

The research for carbon nanotubes started with the interest in the theoretical prediction which was published in 1992 for the special state of electrons in carbon nanotubes.(5) Then after 1996 the theoretical research for the physical property of carbon nanotubes came into bloom all at once with the rapid improvement of the technology for the experiment of measuring carbon nanotubes. Besides, the various applications for these materials have been proposed, and this seems to affect the development of nanotechnology a great deal.

The progress of the technology for measuring materials on a nano-size scale seems to be faster than the development of the study of carbon nanotubes. The materials on a nano-size scale belong to the domain where the special quantum effect (see page 35)

Figure 7

Carbon nanotubes as the probe needle of scanning probe microscopy

Photo: Seiko Instrument Inc.

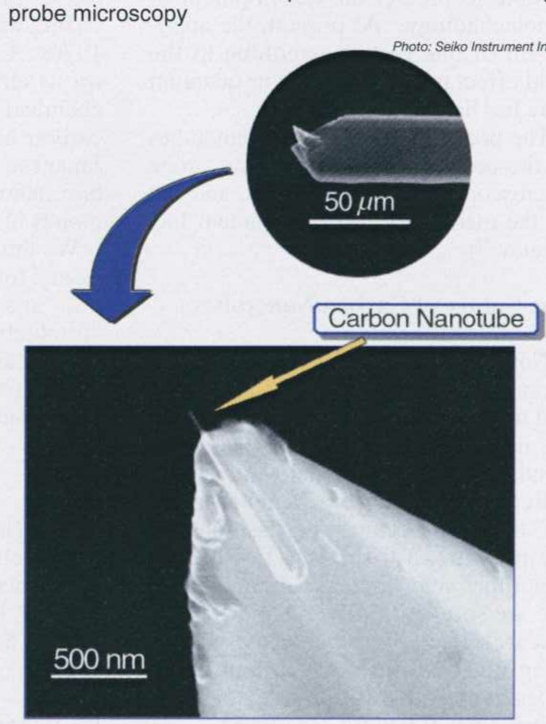
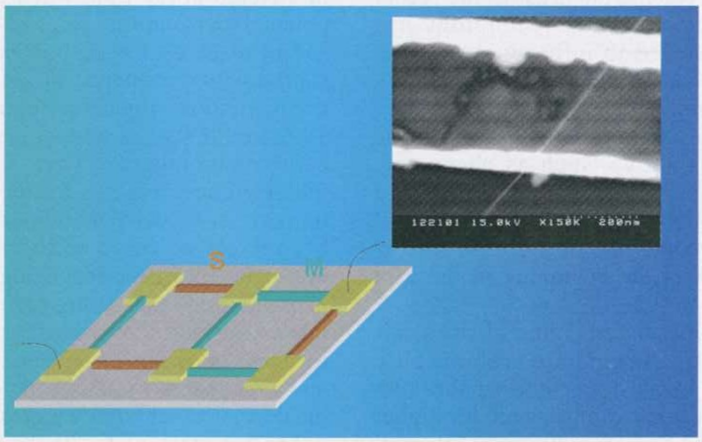


Figure 8

Nanotube device

Left: Concept of the nanotube circuit

Right: Scanning electron microscope image of nanotube on the silicon electrode



appeared, on which the characteristics of the reflection of the wave function of the electron can be observed.

Therefore, in order to utilize this quantum effect, we have to investigate the application of carbon nanotubes. By observing the development of the research for carbon nanotubes, we may be able to predict the development of nanotechnology. At present, the application of one carbon nanotube to the field effect transistor (FET) or quantum wire has been proposed.

The practical use of carbon nanotubes as the probe needle of scanning probe microscopy has already begun, and put on the market by Seiko Instrument Inc. (Figure 7)

The Future of Carbon Nanotubes

Now is the time of the "rise of nanotechnology," and, it might be stereotypical to say, but this technology is one of the most advanced technologies in the trends of technological innovation.

Recently, as the word "nanotechnology" itself has become very fashionable, the pressures for the R&D of carbon nanotubes may increase dramatically. We are sure that profound and flexible research itself is the shortest way to open up the future of "carbon nanotubes" and make it possible for us to develop nano-devices. (Figure 8)

However, all the researchers involved in carbon nanotube research in Japan may have a wish not to make carbon nanotubes as short-lived topical new materials, but to keep developing the research in order to make this material useful for mankind.

Coal, a material that was given the name "black diamonds" because of its value was used in Japan until the 1970s. Coal supported Japanese industry as an energy source and also as a chemical feedstock. We are sure that carbon nanotubes will widely support Japanese industry. We believe that carbon nanotubes will be the "black diamonds of the 21st century."

We think that such enthusiasm is necessary for the development of "materials," and we know that "devices" and "products" are made from "material." When carbon nanotubes fully become useful for mankind, our mission will have been fulfilled. JJTI

Notes

(a) C_{60}: New round-shaped carbon materials which are composed of 60 carbon atoms, discovered by such researchers as Harry W. Kroto of the United Kingdom and Richard E. Smalley of the United States in 1985.

(b) Vapor grown carbon fiber (VGCF): Normally, carbon fibers are produced by; 1) weaving PANs (polyacrylonitrile), pitches or other materials, and 2) go through heat treatment. VGCF, on the other hand, are produced by 1) resolving hydrocarbon such as benzene by heated vapor and 2) by synthesizing them.

References

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