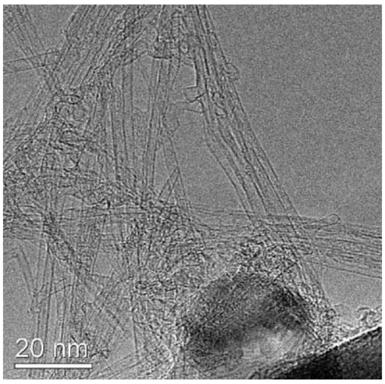

Development of Fabrication Technology of Carbon Nanotube by Fluidized-bed Reactor

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1. Introduction

Various applications are proposed for single-wall carbon nanotube (CNT: carbon nanotube) bacause of its remarkable physical properties such as high electro-conductivity, strength and so on. However, with the present fabrication method using laser abrasion method, arc discharge method and pneumatic transportation reactor, it is hard to scale up their fabrication processs. As a result, the high-purity single-wall CNT (low in cost and stable in quality) was not easily available, so that its application was limited. Hence, a mass-production technology for single-wall CNT was developed in this research by using fluidized-bed reactor suitable for continuous mass fabrication.

2. CNT and the fabrication method

2.1 CNT and its application

CNT is a tube-like substance with the tube wall made up of hexagonal carbon network (graphen sheet)(1). **Fig. 1** shows the model diagram of CNT. There are different types of CNT with the tube wall ranging from single-wall to several-wall, say dozens of wall. The one with single wall in Fig. 1 is called single-wall CNT, and the one with more than two walls is called multi-wall CNT.

The features of single-wall CNT given in **Table 1** are: high electro-conductivity, high mechanical strength, high heat resistance and so on. The single-wall CNT has now become one of the key materials for new products in the fields of display application, semiconductor application, etc. in addition to the application as a substitute to conventional carbon materials such as elecrtro-conductive filler to the resin, etc.

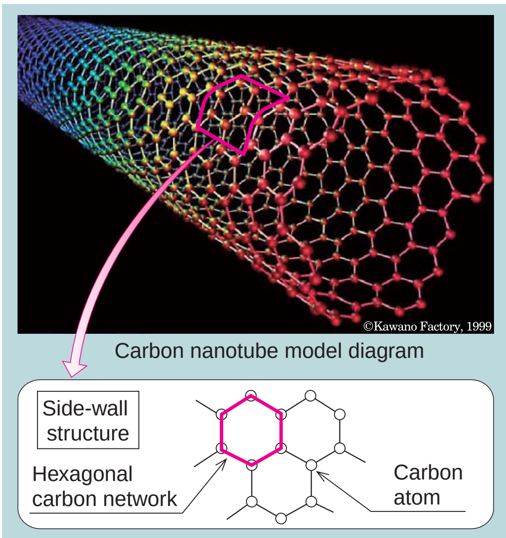

Fig. 1 CNT model diagram
CNT has the structure of hexagonal carbon network (graphen sheet) rolled into the shape of a tube.

Table 1 Features and applications of CNT

Application	Features for use	Merit	Development level
Electro-conductive filler for resin-structure material	• Formation of high-conductivity network • Nano size	• High electro-conductive performance by slight addition → Maintenance of base metal physical properties and improvement in resin recycling	• Commercialized
Electron emission source for FED application, etc.	• High-conductivity • Extra-fine (easy electron emission)	• Electron emission possible at low voltage and low temperature → Reduction of power consumption	• Trial-manufacture
Battery electrode material	• Formation of high-conductivity network • High specific surface area (for support of catalyst)	• Low resistance and low-temperature operation • Improvement of battery output	• In actual use (Li-ion battery) • Trial-manufacture (fuel cell)
Field-effect transistor (FET)	• High electron mobility (10 times that of Si)	• High-speed, high current density transistor to replace Si	• Basic development
LSI veer wire	• High electro-conductivity and current density • High thermal-conductance	• Restriction of heat generation at high integration	• Basic development

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2.2 Fabrication method

Fabrication technology for single-wall CNT using fluidized-bed reactor was developed, with the model fluidized-bed reactor shown in **Fig. 2**. The fluidized-bed reactor is formed by supplying CNT raw material (hydrocarbon gas) into the catalyst particles through the bottom of the reactor. When reacted at specified temperature, the single-wall CNT grows starting from the active metal of the catalyst. The high purity single-wall CNT powder can be obtained by removing the catalyst.

The fluidized-bed reactor has the features given below.

(1) It is easy to control the catalyst particle diameter on the catalyst support and to manage the selectivity of the single-wall CNT growth.

(2) The particles mix well, the reaction atmosphere is highly uniform and the quality of single-wall CNT is highly stable.

(3) It is easy to handle the supply and discharge of solid particles.

These features of the fluidized-bed reactor enable continuous production of CNT, ensuring stable and high productivity of high-purity single-wall CNT.

3. Production test results of single-wall CNT using fluidized-bed reactor

Study was conducted on the fabrication of single-wall CNT using fluidized-bed reactor with the test conditions for fluidized-bed reactor summed up in **Table 2**. The catalyst was supplied continuously at the rate of 6.4 kg/h, continuously discharging the catalyst particles adhered with single-wall CNT from the catalyst particle removing hopper, with the single-wall CNT production rate being 140 – 250 g- CNT/h.

Fig. 3 shows the image of scanning electron microscope (SEM) of the obtained sample, indicating the confirmed growth of extra-fine fibers on the catalyst surface. An observation using transmission electron microscope proved that these fine fibers were single-wall CNT with diameter 1 – 3 nm (**Fig. 4**).

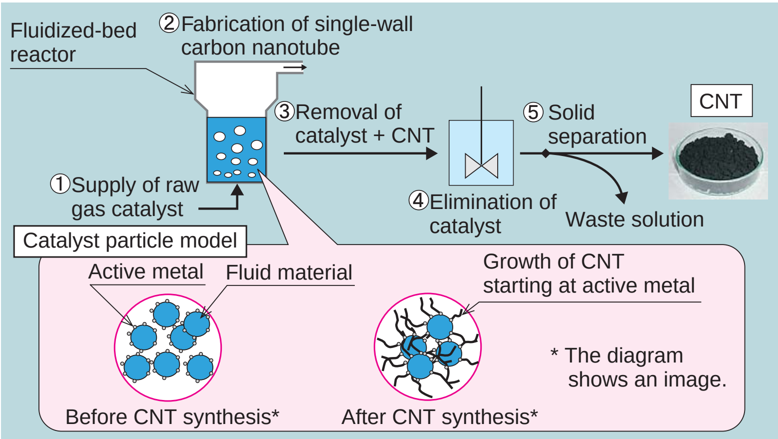

Fig. 2 Model diagram of fluidized-bed reactor
CNT is fabricated in processes (1) – (5). Catalyst particles were used as the fluid material to be fed in the fluidized-bed reactor.

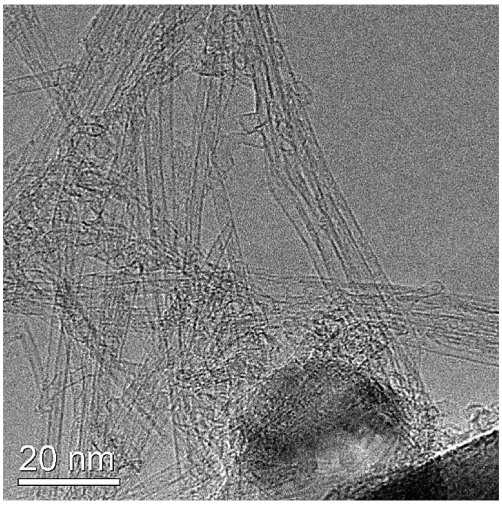

Fig. 4 Transmission electron microscope (TEM) image of the sample experimentally manufactured by using continuous fabricating fluidized-bed test equipment (reactor)
Black stripe patterns caused by carbon element are confirmed, with the space between patterns in correspondence with the tube external shape being 1– 3 nm, indicating the synthesis of single-wall CNT.

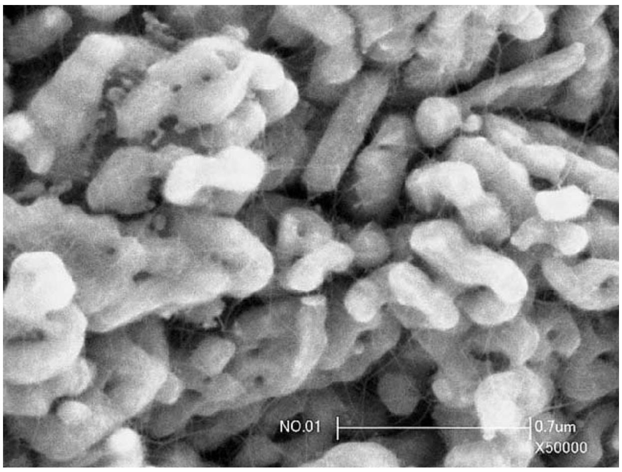

Fig. 3 Image of scanning electron microscope (SEM image) of the sample experimentally manufactured by using continuous fabricating fluidized-bed test equipment (reactor)
After fabrication of CNT, extra-fine fiber with diameter <10 nm is confirmed on the catalyst surface.

Table 2 Test conditions for continuous fabricating fluidized-bed test equipment (reactor)

Reactor	Continuous fabricating fluidized-bed test equipment (reactor)
Catalyst	Fe type
Catalyst supply unit	6.4 kg/h
Catalyst support	Magnesium oxide (MgO)
Supply gas	CH_4=20 %, N_2=80 %
Pressure (MPa)	0.1
CNT fabricating temperature (°C)	800
Fluidized-bed size (mm)	Diameter: 151, bed height: 150

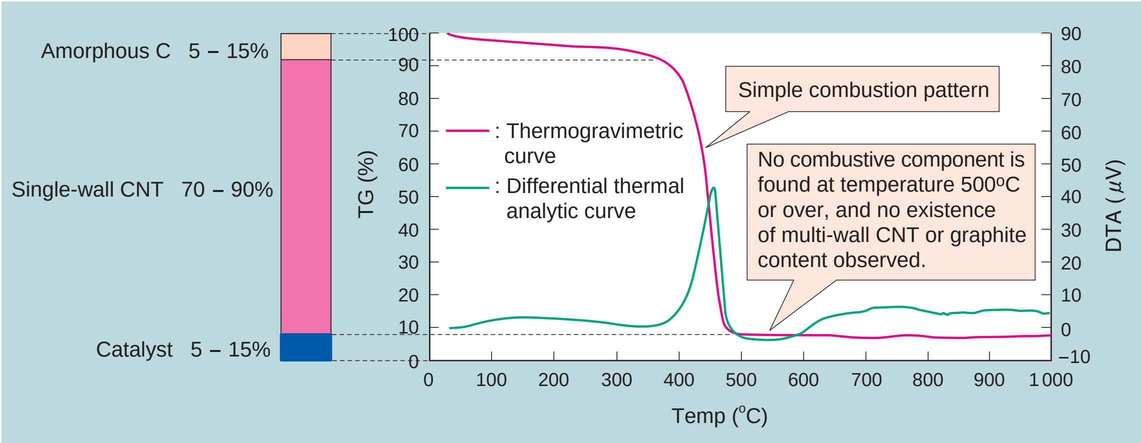

Fig. 6 Analysis result of thermogravimetry (TG-DTA) and purity evaluation of the sample experimentally fabricated by using continuous fabricating fluidized-bed test equipment (reactor)
The weight changes at continuous temperature rise recorded the weight reduction of 70 – 90% between 400 – 500°C, the combustible calcinations 5 – 15% and catalyst residue 5 – 15% at 400°C or under:

Besides, it was confirmed through Raman spectroscopy in **Fig. 5** that the radial breathing mode (RBM) specific to the single-wall tube structure was observed at the region 300 cm^{-1} or under. The purity of the single-wall CNT was evaluated by thermogravimetry. The result from **Fig. 6** showed a sharp weight reduction of 70 – 90% to correspond to the single-wall CNT at about 450°C as well as the subsequent exothermic peak. The combustible calcinations ratio at 400°C or under was found to be 5 – 15% and 5 – 15% catalyst residue at 500°C or over. It was confirmed through these results that single-wall CNT of purity 70 – 90% was continuously produced in the fluidized-bed test equipment for continuous manufacture.

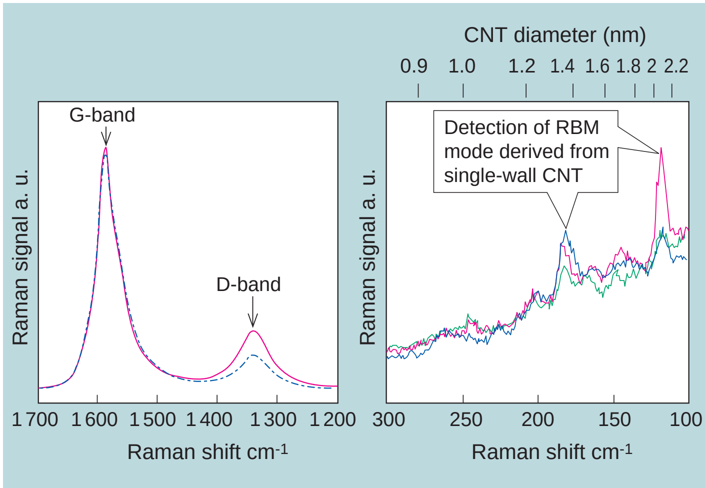

Fig. 5 Raman spectroscopy of the sample experimentally manufactured by using fluidized-bed test equipment (reactor)
Signals from G-band due to graphite and RBM derived from single-wall CNT were confirmed, indicating the existence of single-wall CNT in the sample.

4. Conclusion

Mitsubishi Heavy Industries, Ltd. (MHI) has succeeded for the first time in the world in continuous fabrication of single-wall carbon nanotube, ensuring effective manufacture of single-wall carbon nanotube by applying catalyst of special structure to MHI fluidized-bed reactor. The productivity at the present stage is 140 – 250 g/h and the purity of the single-wall carbon nanotube is 70 – 90%. In the future, MHI plans to demonstrate the annual production of several tons for fiscal year 2007, and to realize a drastic cost down as compared with the convention sample market price, aiming at the expansion of application to the business of materials and their applied products.

This research was a part of the advanced nanocarbon application project consigned by the New Energy and Industrial Technology Development Organization (NEDO) to the Japan Fine Ceramic Center (JFCC).

References

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