Carbon Nanotube Technology

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Abstract

The carbon nanotube (CNT) is a representative nano-material discovered in 1991 at NEC. With its unique structure, high strength, high electric conductivity and high thermal conductivity, CNT is expected to be applied widely together with its variant the carbon nanohorn (CNH) in electronic devices such as transistors and fuel cells as well as in the environmental and biotechnological fields. This paper introduces the characteristics and features of CNT and CNH and describes some of their application fields.

Keywords

carbon nanotube, carbon nanohorn, transistor, fuel cell, drug delivery system

1. Introduction

The carbon nanotube (CNT) is a representative nano-material. As a result of its unique form and features, CNT is expected to find application together with its variant the carbon nanohorn (CNH) in a wide range of fields.

In this paper, we will explain the characteristics and features of these materials and introduce some of their application fields.

2. Features of CNT

CNT is a cylindrically shaped carbon material with a nanometric-level diameter. Its structure, which is in the form of a hexagonal mesh, resembles a graphite sheet and it carries a carbon atom located on the vertex of each mesh. The sheet is rolled and its two edges are connected seamlessly. Although it is a commonplace material that is used in pencil leads, its unique structure causes it to present characteristics that are not found with any other materials. CNT can be classified into single-wall CNT, double-wall CNT and multi-wall CNT according to the number of layers of the rolled graphite. The multi-wall CNT was discovered in 1991[1)] and the single-wall CNT in 1993[2)]. The type attracting most attention is the single-wall CNT as shown in **Fig. 1(a)**, which has a diameter deserving the name of "nano"tube of 0.4 to 2 nanometers. The length is usually in the order of microns, but single-wall CNT with a length in the order of centimeters has recently been released.

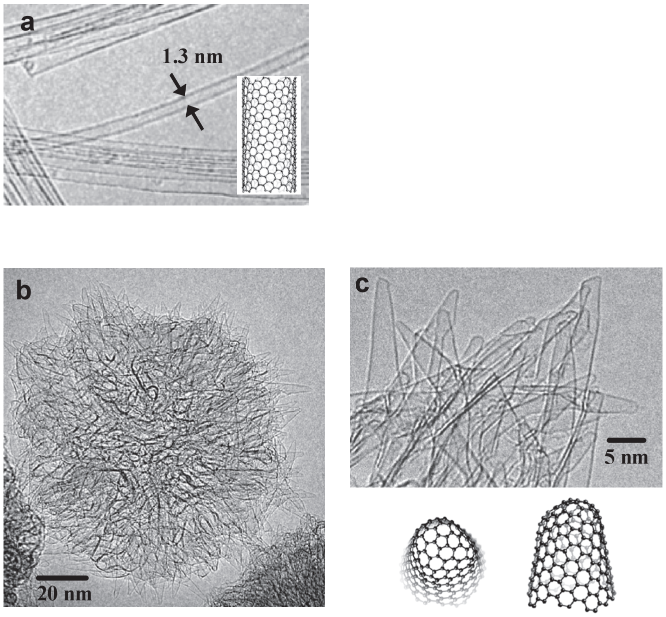


Fig. 1 Transmission electron microscopy images of CNT (a) and CNH (b), (c). Inserted illustrations are CG images of CNT and CNH respectively.

The extremities of the CNT are usually closed with lids of the graphite sheet. The lids consist of hexagonal crystalline structures (six-membered ring structures) and a total of six pentagonal structures (five-membered ring structures) placed here and there in the hexagonal structure. A soccer ball surface is composed of 20 hexagonal patterns and 12 pentagonal patterns, and this number of pentagonal patterns is necessary for making the ball shape spherical. It is because each lid of CNT is a hemisphere that the number of pentagonal patterns on it is 6.

3. Features of CNH

CNH is a nanometric carbon tubes taking a horn or cone shapes at the tip. This material has five five-membered rings on the extremity of the horn. As shown in the transmission electron microscopy images shown in **Figs. 1(b) and (c)**, some thousands of horn structures are usually assembled into a spherical shape by orienting their extremities toward the outside and this shape somewhat resembles a chestnut bur or a sea urchin. This assembly has a diameter of from 80 to 100 nanometers. The CNH structure is distorted due to the presence of some five- or seven-membered rings, but the assembly is stable because these structures are bonded at the center.

4. Synthesis of CNT and CNH

CNT is made of a compound containing graphite and carbon and synthesized using transition metals such as iron or nickel as the catalysts. Synthesis from graphite is possible using either an arc discharge or laser ablation technique. The arc discharge process produces CNT by sparking arc discharges in an inactive gas such as helium using graphite rods containing catalysts as the electrodes. The laser ablation process synthesizes CNT by irradiating a pulsed YAG laser on a graphite rod containing catalysts heated to 1,000°C or higher. The diameter of the CNT can be controlled by varying the type and ratio of the catalysts or the ambient temperature. CNT can also be synthesized from a carbon compound by means of chemical vapor deposition (CVD). The CVD process synthesizes CNT by thermally decomposing carbon hydride or alcohol using catalysts at a relatively low temperature (for example 800°C). This process has been advanced rapidly in recent years.

Laser evaporation can also be used in the synthesis of CNH, but it is not necessary to add the metal catalysts to the graphite rod. In addition, neither is it necessary to heat the graphite rod when irradiating by laser (the CO_2 laser is usually used). As a result, this process can synthesize a large amount of high-purity CNH at a relatively low cost.

5. Applications of CNT

Each of CNT and CNH has special properties and R&D is currently being actively conducted in order to apply these properties to products (**Fig. 2**). The properties of CNT vary between those of semiconductors and those of metals depending on the tube diameter and chirality (how the graphite sheet is rolled). This variation occurs because the diameter of the CNT is very small, at the nano-meter level. The graphite is characterized as semimetal and is originally a highly conductive material. When it is formed into a very small cylinder, the electrons moving in the circumferential direction are limited by a quantum mechanical effect and this quantization causes two thirds of the CNT to be a semiconductor. Because the graphite that originally had good electrical characteristics acquires the properties of a semiconductor and that the electrons moving in the axial direction of the cylinder are scattered less by impurities, etc., the CNT acquires characteristics that are favorable as a transistor material.

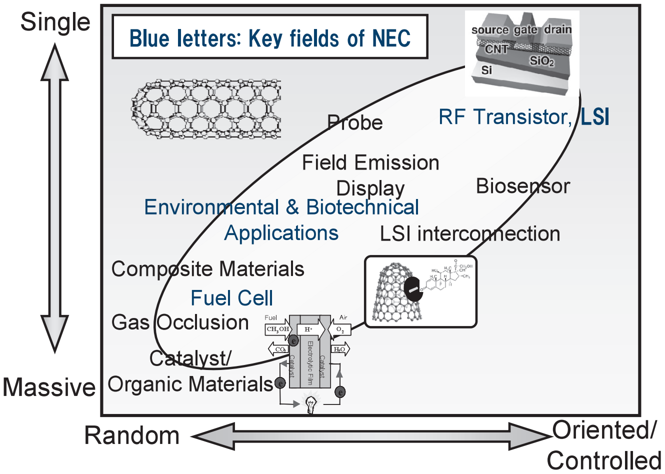


Fig. 2 Application map for CNT and CNH.

There are also other features that make it a favorable transistor material. The transistor has three electrodes named; source, drain and gate and functions as a switch according to the electron density of the semiconductor channel between the source and drain, which is controlled by the voltage applied to the gate electrode (**Fig. 3**). It is known that the control through the gate electrode can be improved by using a material with a high dielectric constant in the insulation film between the semiconductor channel and the gate electrode or by fabricating the gate electrode so that it surrounds the semiconductor channel. The insulation film usable with ordinary semiconductors such as silicon has limitations due to its unstable surface but the CNT has a stable surface so that a large variety of insulation film materials can be used with it. In addition, the structure of CNT makes it easy to fabricate the gate electrode so that it surrounds CNT.

NEC fabricated a transistor that uses a CNT as the channel in order to investigate the potential of CNT as a transistor mate-

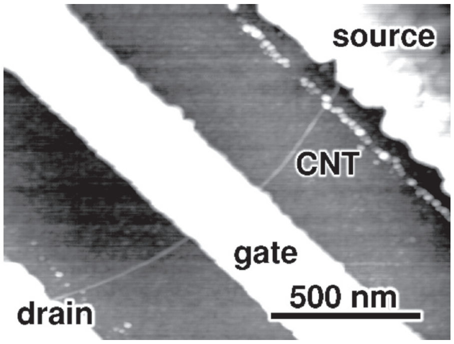


Fig. 3 Scanning probe micrograph of CNT transistor.

rial, and examined the characteristics of the transistor[3] (**Fig. 4**). We prepared the catalyst on the silicon substrate by using the micro-fabrication technology and synthesized a single-layer CNT with the CVD process. The gate material of this transistor was titanium dioxide, which has not been used with the silicon material due to poor affinity.

An important feature of transistors is how far the input voltage can control the output current. This characteristic is represented with the output current variation per input voltage and is referred to as trans-conductance. We measured the trans-conductance of the CNT transistor and found it was as high as about 10 times that of the transistor with an advanced silicon transistors (Fig. 4). We therefore expect that the CNT transistor can be a promising candidate to support the nano-electronics in the future.

Another development of CNT as a transistor material is based on the fact that CNT can be dispersed in an organic solvent and the solution can be used as a transistor when it is used to coat various kinds of substrate. It has been reported that a transistor formed in this way on a plastic substrate functions well even when the substrate is bent. This means that CNT has potential as a material for applied products, a feature that has not been possible with traditional silicon electronics.

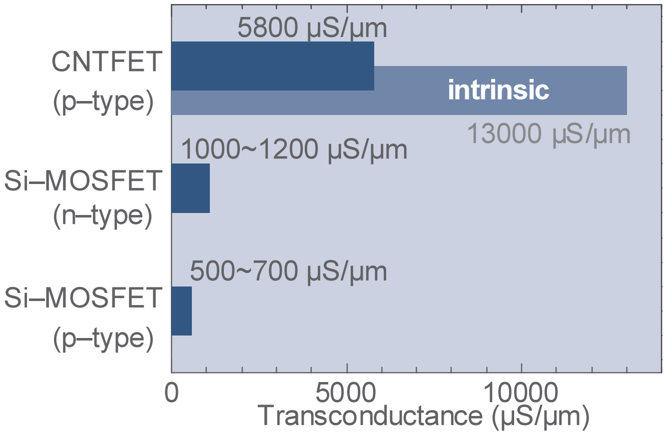


Fig. 4 Comparison of trans-conductance between CNT transistor and silicon devices (n-type and p-type).

The transistor is only one of the possible applications of CNT. Other applications include the field emission display, mode-locked laser device, anti-charge plastics and reinforced plastics. Some of these have already been commercialized. The importance of this material demands that we consider its future development with a careful eye.

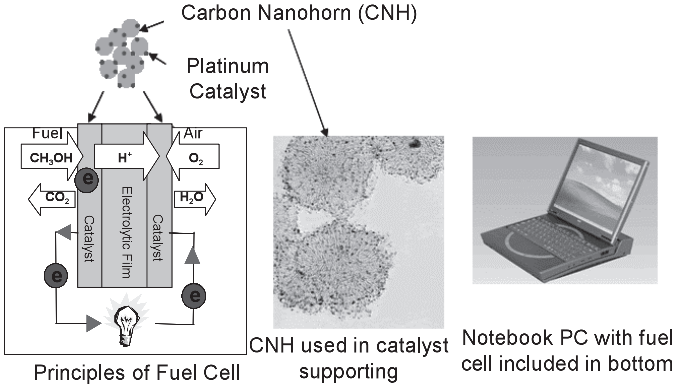
6. Applications of CNH

Like the single-layer CNT, CNH is formed by a single-layer graphite sheet, and the inside of the CNH is hollow. When CNH is heated in an oxygen atmosphere, the holes are put in the walls, and the size and number of these holes are controlled according to the temperature and the length of time of heating. Through the holes materials enter inside the CNH where they are stored.

NEC put small Pt particles on CNH and used the Pt loaded CNH as the electrode of a fuel cell and succeeded in increasing its output power (**Fig. 5**). The fuel cell generates power by separating the methanol fuel into hydrogen ions and electrons, where platinum works as the catalyst. The surface area of platinum particles can be increased by using CNH because this can finely separate platinum at the nanometric level and attach it on the outside the CNH. If an ordinary carbon material with a smooth surface is used, the attached platinum size becomes large, and the surface area per unit wait of platinum as well as the catalysts effect reduce. Using CNH electrodes with such a platinum supporting capability, we succeeded in achieving the world's highest output density of 100mW/cm^2 with a direct methanol fuel cell.

Collaboration between NEC, the Japan Science and Technology Agency and the Cancer Institute of JFCR (Japanese Foundation for Cancer Research) has succeeded in including the anticancer drug “Cisplatin” in CNH. This achievement shows the potential of CNH for use as an anticancer drug carrier of a drug delivery system (DDS) targeting cancer cells. DDS is the technology for delivering a drug exclusively to the target infected region. Such a pinpoint drug delivery capability is attracting attention because it can quantitatively minimize drug administration, increase the effect and reduce side-effects.

Cisplatin is incorporated in CNH via the holes created in the graphene wall, and the amount of inclusion can reach as high



Principles of Fuel Cell

CNH used in catalyst supporting

Notebook PC with fuel cell included in bottom

Fig. 5 Fuel cell using CNH.

as about 10-20% of the weight of the CNH. Our transmitted electron micrograph in **Fig. 6(a)** shows that the included Cisplatin forms clusters of about 2 nanometers while maintaining its original molecular structure. We actually added CNH including Cisplatin in a container culturing cancer cells and confirmed that the Cisplatin gradually emitted from the CNH killed the cancer cells[4]. The death rate of the cancer cells varied depending on the concentration of the Cisplatin-including CNH as shown in **Fig. 6(b)**.

Past animal tests and cell tests have shown that CNH does not have a short-term toxicity to the living body and can be a safe carrier that does not affect the surrounding cells and tissues. The CNH including the anticancer drug would be delivered to tumors with blood, because the tumor blood-vessels are leaky and substances with sizes of about 100 nanometers are invaded from the blood vessels to the tumor. We believe that CNH can play an important role as a drug carrier and are currently conducting research along these lines.

7. Conclusion

CNT and CNH have features that are not found in traditional materials. This paper has explained the characteristics and features of these materials and introduced their applications in transistors, fuel cells and in drug delivery systems (DDS). An active search is underway for new materials including nanomaterials and it is expected that the discoveries will lead to various applications. NEC aims to resolutely advance R&D that can contribute to the advancement of humankind while at the same time maintaining a harmonious relationship with society.

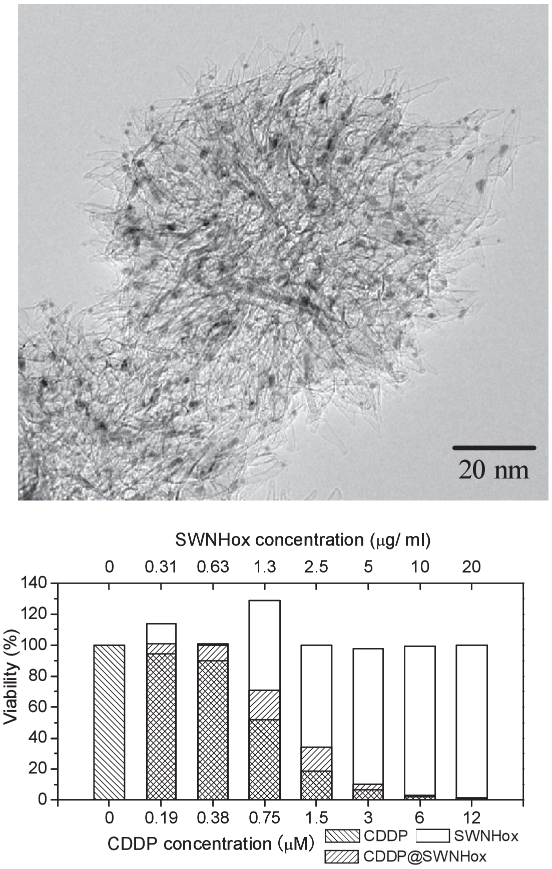


Fig. 6 (a) Transmitted electron micrograph showing inclusion of Cisplatin (CDDP) Clusters (Black dots) in Holed CNH (Referred to as “SWNHox” here). (b) When CDDP, CDDP-including SWNHox and non-CDDP-including SWNHox are administered (in vitro) in human lung cancer-derived cell stocks (H460), the cell survival rate is dependent on the concentration. The CDDP-including SWNHox causes the cancer cells to decrease as the concentration increases.

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