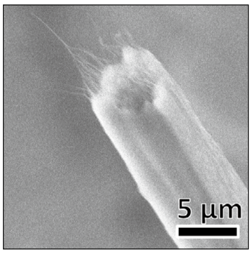

Ultra-High Strength Carbon Nanotube Yarn Made by New Growth Method

Soichiro OKUBO*, Takeshi HIKATA, Toshihiko FUJIMORI, Daisuke TANIOKA, Daiji YAMASHITA, and Takamasa ONOKI

We have been focusing on carbon nanotubes (CNTs) as a material for next-generation electric wires that are lighter and more conductive than copper and aluminum wires. CNT single fiber has a greater conductivity than copper and the highest tensile strength of any known material. Aiming at the practical application of CNT electric wires, we have discovered the effectiveness of applying tensile stress to CNTs during the growing process from iron catalysts. In addition, at the University of Tsukuba, where a joint research was conducted, the growth of centimeter-class single fibers was observed in high-speed airflow, suggesting that stress applied during the growth contributes to the lengthening of CNTs. Using this principle as a basis for the growth method, we have created a metric-class CNT yarn that aggregates these long CNT single fibers. The new yarn has several times the strength of the conventional CNT yarn and exceeds the tensile strength of commercially available carbon fibers. This yarn will not only replace carbon fibers but also create new applications that have never been seen before.

Keywords: carbon nanotube, yarn, honeycomb, high-velocity gas flow

1. Introduction

Carbon nanotubes (CNTs) are made only from carbon. A single fiber has a cylindrical structure, which is made by rolling a sheet of six-membered rings of carbon atoms. CNTs are lighter than aluminum, and their tensile strength is 20 times or more that of steel. They are also expected to have properties, such as high electrical conductivity, surpassing that of copper. CNTs are lightweight because their specific gravity is one fifth that of copper. Their chemical durability is also high. Deformation with a large curvature, which could not be attained with conventional carbon fibers, is feasible.(1) Thus, CNTs are expected to be used as next-generation electric wire materials to cope with the shortages of copper and reduce the weight of electric wires used in vehicles. Studies have been conducted to use CNTs as electric wire materials, but the electrical and mechanical properties of CNT yarns have not yet reached a level equivalent to those of CNT single fibers. The biggest problem is that it has been difficult to increase the length of single fibers. There is a report that CNT single fibers of up to several dozen centimeters have been fabricated. However, the technique is not suitable for mass production because the yield is very low.(2) There is a mass production technique to fabricate CNTs of 1 cm long. However, it is difficult to control the quality of CNT fibers. In addition, there is a trade-off between quality and length. Namely, CNT single fibers of good quality grow only about several dozen micrometers. There is a different example of producing yarns with continuous growth, but it has been difficult to maintain the orientation of the fibers.

The mechanical strength of CNT yarns has been studied. Numerical values reported by various research groups are shown in Fig. 1, which indicates that the strength of conventional CNT yarns is far below that of a single fiber and even inferior to that of conventional carbon fibers.

To attain practical application for electric wires,

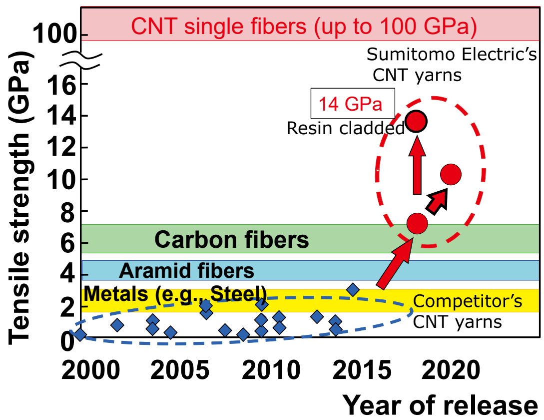

Fig. 1. Changes in the tensile strength of CNT yarns reported in papers and comparison of their strength against Sumitomo Electric's CNT yarns

Sumitomo Electric Industries, Ltd. has studied CNT growth methods that meet the requirements of both long growth of high quality CNTs and orientation of single fibers. CNT yarns fabricated using a newly developed growth technique have attained the highest tensile strength in the world, far exceeding that of previously reported CNT yarns and even exceeding that of carbon fibers. This paper reports the details.

2. Conventional Growth Methods

In 1991, S. Iijima et al. determined the structure of CNTs using an electron microscope and revealed how peculiar it was.(3) Previously, Endo et al. discovered a technology to grow thin carbon fibers in the 1970s. In this technique,(4) metal catalyst microparticles, which served as the starting points, were placed on a substrate and CNTs were allowed to grow by thermal CVD.*1 This technique is used in many mass production processes at present. The substrate method, which was developed under the initiative of the National Institute of Advanced Industrial Science and Technology (AIST), achieved growth of long CNTs of one centimeter, which was the longest at that time. However, it was accompanied by a trade-off between quality and length.(1) The eDIPS method, which is another technique developed by AIST, achieved CNTs with fewer defects with a length of less than 100 µm.(5) However, the yield was below the level for mass production. All of these methods have advantages and disadvantages. At Sumitomo Electric, we discovered that high-purity graphite fibers grew like bridges across thermal cracks generated during gas carbonization of an oxidized iron foil. This was reported as the "bridge growth method."(6) In this growth phenomenon, carbon, which is subject to saturated carburizing in bulk iron, is withdrawn by the tensile force when cracks propagate on a surface. When a pure iron foil is separated during carburizing, high-purity graphite fibers of several millimeters can be withdrawn by optimizing the conditions. This gave us a hint about the phenomenon of continuously extending fiber length in the newly developed CNTs growth method.

3. Overview of the New CNT Growth Method

3-1 Discovery of a new growth phenomenon

To identify the working principle of the abovementioned bridge growth method, we conducted basic research on the carburizing phenomenon jointly with the University of Tsukuba. During the carburizing experiment at the university, we discovered a phenomenon in which many high-quality CNTs of few centimeter with minimal defects grew on a quartz glass substrate placed in a narrow channel (see Fig. 2).

Verification was conducted on this phenomenon, and it was found by simulation that the gas flowed at a high velocity in the narrow channel. The results suggested that tensile stress was applied to CNTs during growth, causing CNTs to grow very long (few centimeter) due to the significant difference in flow velocity from the wall surface to the center of the channel. To further verify the working principle and take a step closer to practical application, we applied for a project under the auspices of the New Energy and Industrial Technology Development Organization (NEDO) jointly with University of Tsukuba, and our proposal was accepted. In the NEDO project, we measured the strength of CNT single fibers at the University of Tsukuba. Regarding the measurement technique, CNTs which grew across grooves on a silicon substrate were exposed to a gas blow. The rupture strength was calculated based on the deflection of the single fibers at the time of rupture.(7) It was found that the strength of the single fibers was equivalent to 100 GPa,(8) which was calculated. In the quality evaluation based on Raman spectroscopy, there were few signals attributed to defects (D peak). This proved that the quality was very high. Based on the peak attributed to the diameter, the diameter of the CNT fibers was found to be about 1 to 2 nm.

3-2 Key to the new CNT growth technology developed by Sumitomo Electric

After it was found that very long high-quality CNTs could be fabricated by using the phenomenon discovered at the University of Tsukuba, Sumitomo Electric started to develop equipment to achieve mass production. We decided to use a ceramic honeycomb, which has been often used as a reduction catalyst support for automotive exhaust gas, as one of the methods for providing many narrow channels. Such honeycombs are inexpensive and commercially available, and can be readily procured. Figure 3 shows the overview of the experiment system. Ten patents have been applied for regarding this technology.

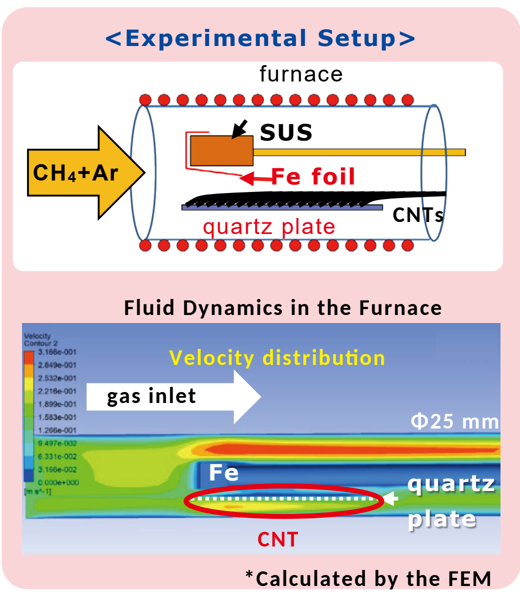

Fig. 2. Schematic diagram of growth of long CNTs in a narrow channel (top) and flow velocity distribution based on calculation (bottom)

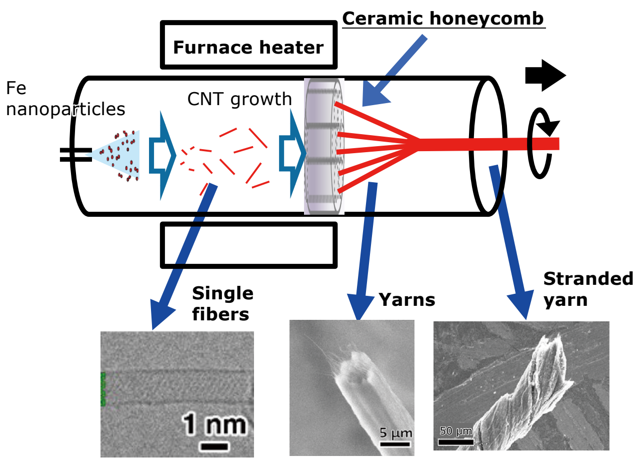

Fig. 3. Schematic diagram of the new growth technique and structure of CNT yarns in respective positions (electron microscopic images)

3-3 Raw materials

Transition metals with high carburizing capacity, such as iron (Fe), nickel (Ni), and cobalt (Co), are often used as catalyst metals, which serve as the starting points of growth of CNTs. The process of Sumitomo Electric also used Fe as a catalyst, as in the case of conventional techniques. A ferrocene solution was used as the Fe source. The ferrocene solution was atomized from the inlet of the electric furnace. Methane (CH_4) and hydrogen (H_2) were fed as a raw material gas and a carrier gas, respectively, at a certain flow rate. The atomized ferrocene solution mixture was carried with the gas flow to the high-temperature reaction zone and was turned into Fe metal nanoparticles through thermal decomposition reaction. The raw material gas was thermally decomposed for carburizing.

3-4 CNT growth process

The basic growth process is a thermal CVD growth method, which is conventionally used for CNT growth (so-called "Floating Catalyst Method"). An Fe raw material solution, which would turn into catalyst nanoparticles, was atomized in a tubular electric furnace at about 1,000°C. A hydrocarbon-based raw material gas and a carrier gas were fed at the same time and were thermally reacted in the high temperature zone. CNTs were continuously taken out from the outlet on the opposite side.

Regarding the working principle of CNT growth in this technique, carburizing is performed using the CH_4 gas as a carbon source against catalyst particles (e.g., metal Fe), which are present as nanoparticles at high temperature. Surplus carbon grows as CNTs in stages from particles that are subjected to saturated carburizing. Carbon, which is removed from particles as CNTs, is supplied from the raw material gas. This cycle enables continuous growth of CNTs. The diameter of the CNTs is the same as the diameter size of the nanoparticles. In the conventional catalystic CVD method, amorphous carbon accumulates on the surface of nanoparticles concurrently with carburizing. Thus, the supply of carbon from the gas decreases gradually, and the growth of CNTs stops. This is considered to be the reason why only short single fibers can be obtained.

In our technique, CNTs, which are in a growth process, grow while being carried with catalyst nanoparticles in a high-velocity gas flow in a narrow channel. The CNTs are subjected to tensile stress due to the significant difference in the gas velocity that is in the direction perpendicular to the flow direction. Thus, carbon is withdrawn continuously, and carbon concentration in particles is balanced at the saturated level. This is considered to inhibit the growth of amorphous carbon on the surface.

As discussed above, a commercially available ceramic honeycomb was used as a method of providing many narrow channels to achieve continuous CNT growth in large quantities. A ceramic honeycomb of about φ50 mm was used to fit into the furnace core tube. The channel shape was 1 mm to 3 mm square (see Photo. 1).

The quality of the CNTs which were allowed to grow through the honeycomb was identified by Raman spectroscopy. The profile showed that the G peak attributed to the six-membered rings of carbon was very high and that the D peak attributed to defects was very low. It was found that the quality was as high as that of CNTs that were allowed to grow in the basic study (Fig. 4).

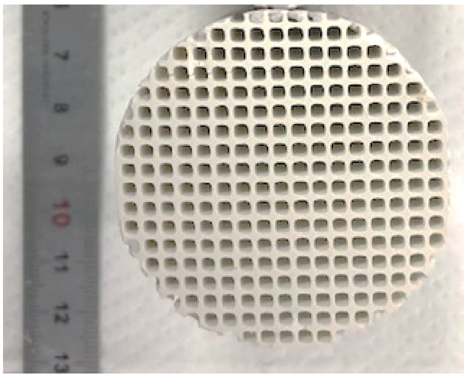

Photo 1. Cross section of a honeycomb used for growth of CNT yarns

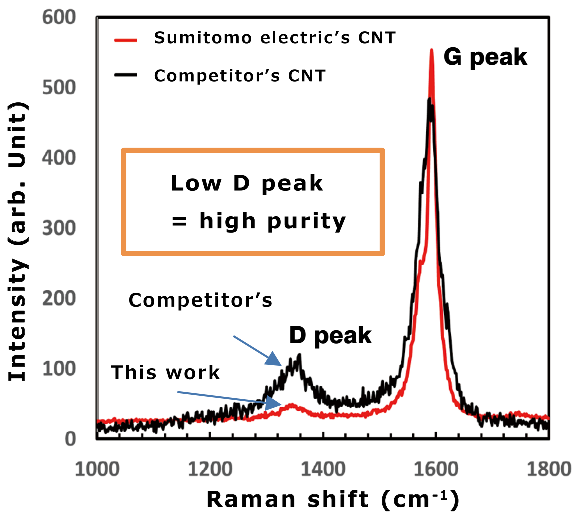

Fig. 4. Results of Raman spectroscopy on CNT yarns manufactured using a honeycomb

The element yarns were confirmed to be oriented in one direction, as shown in Fig. 5, based on electron microscope observation of the surface. CNTs obtained using the honeycomb and without using the honeycomb were subjected to electron microscope observation, and element yarns were subjected to orientation evaluation by polarized Raman spectroscopy. The honeycomb was found to be effective in promoting the orientation of CNT single fibers.

The orientation evaluation by polarized Raman spectroscopy aims to obtain a profile at certain angle intervals while emitting a linearly polarized exciting light in a direction perpendicular to the longitudinal direction of a yarn and rotating the polarization plane, and to determine the angle dependence of the G peak strength. This technique was used to measure yarns which were stranded in the following process. A strength peak was observed every 60°. Thus, it was considered that the CNT fibers were oriented in the longitudinal direction and that the rotation angle when the yarns were stranded was reflected (see Fig. 6).

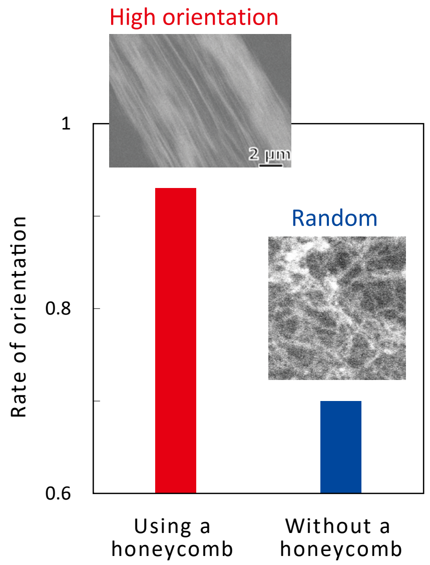

Fig. 5. Evaluation of the rate of orientation of CNT element yarns (measurement by polarized Raman spectroscopy)

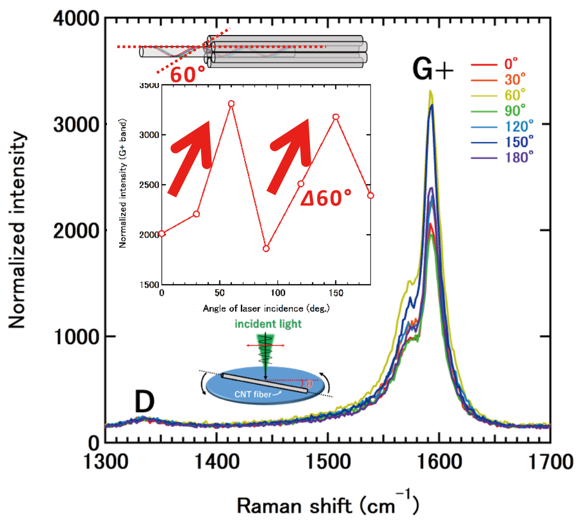

Fig. 6. Results of orientation analysis of stranded yarns by polarized Raman spectroscopy

3-5 Measurement of tensile strength

The strength of the obtained CNT yarns was measured based on a method specified in JIS R1657:2003 "Testing Methods of Continuous Ceramic Fibers for Continuous Fiber-Reinforced Ceramic Matrix Composites." The results are shown in Fig. 7. The tensile strength of CNT yarns which was reported previously was up to 3 GPa, which was below the strength of conventional carbon fibers (7 GPa at the maximum). However, the CNT yarns fabricated using the newly developed technique attained 6 GPa or more with good reproducibility. Resin-impregnated yarns attained about 14 GPa, which far exceeded the tensile strength of conventional carbon fibers. The highest strength in the world was attained for CNT yarns. Stranded yarns exhibited a decrease in tensile strength, but it was found that elongation can be increased. Post-processing after fabrication of yarns demonstrated that tensile strength and elongation are controllable.[9] Subsequent process development also achieved winding of yarns up to about 1 m. Appropriate post-processing attained tensile strength of 10 GPa or more with good reproducibility. This process has made it possible to produce CNT yarns of up to 1 m by continuous growth in manual operation. We have taken the first step toward a mass production process (Photo 2). We also conducted a demonstration to lift a weight by bundling the yarns (Photo 3).

Based on these results, larger-scale equipment is under development with support from the Security Technology Research Promotion System of the Acquisition, Technology & Logistics Agency (ATLA).

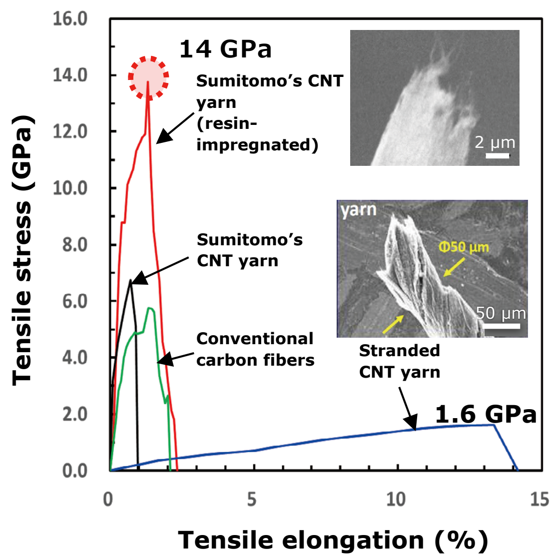

Fig. 7. Results of a tensile strength test on CNT yarns

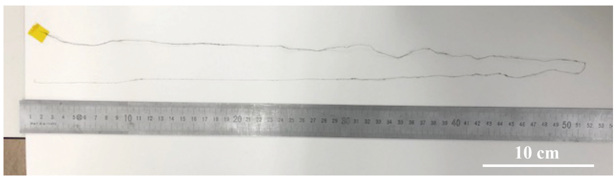

Photo 2. CNT yarn resin composite material (1 m long)

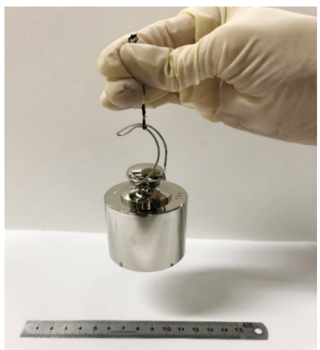

Photo 3. CNT yarn of φ0.4 mm capable of lifting a load of 1 kg

4. Application of CNT Yarns as Yarn Materials and Composite Materials

Based on information obtained through interviews with experts, when the strength of fibers used for fiber-reinforced plastics (FRPs)*2 is increased, this strength is considered to be added to the overall strength of the FRP composites. By using Sumitomo Electric's high-strength CNT fibers, it is possible to achieve FRPs with reduced thickness for the same strength. Such FRPs can be knotted like fishing lines because they can be bent more sharply than carbon fibers (see Fig. 8).

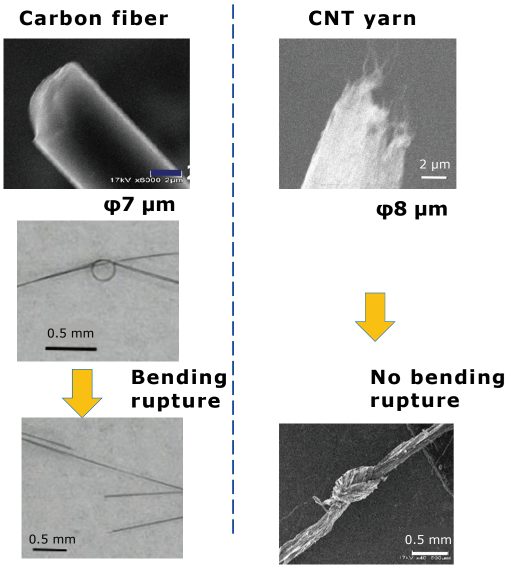

Fig. 8. Difference in flexibility between carbon fibers and CNT yarns

Regarding conventional carbon FRPs (CFRPs), carbon fiber woven cloth is laminated in layers manually into complicated shapes, such as bicycle frame joints, and is impregnated with resin. CNT woven cloth is resistant to deformation into irregular shapes by pressing. This increases the flexibility of the molding process.

The use of CNT yarns for current applications of aramid fibers is expected to increase their strength significantly. Steel cords are used for the reinforced fibers of tires. Because aramid fibers are also used in part, there is a potential market to replace these fibers. Steel is used as the concrete reinforcement material for buildings. The use of CNT yarns offers the advantages of weight reduction and high strength.

The market for existing carbon fibers is expected to reach about 400 billion yen annually in 2025. The market for CFRPs is expected to grow to about three trillion yen, mainly for structural materials for cars and aircraft. These markets are expected to grow significantly into the future.[10] The aviation industry has been shrinking recently due to the COVID-19 pandemic, but the market is expected to recover after the pandemic. There is another potential application in the future. The main structural material for a space elevator*3 called a "tether" (cable) can only be achieved by CNTs due to the specific strength in design.[11] There are high expectations for ultra-high-strength CNT yarns (Fig. 9).

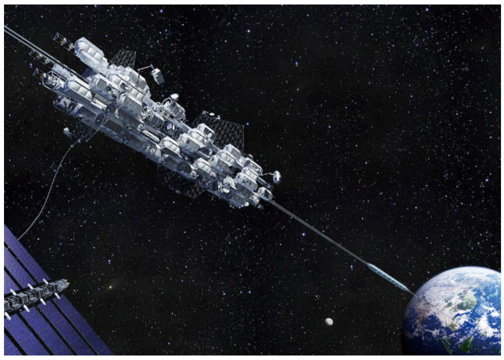

Fig. 9. Conceptual figure of a space elevator
(Courtesy of Obayashi Corporation)

We have been involved in technology development under a national project. Figure 10 shows the future deployment of technology to Sumitomo Electric products and the product development schedule. The technology to achieve high-quality, ultra-long, and high-orientation CNT single fibers for high-strength wires is an essential elemental technology to achieve high strength and high electrical conductivity for CNT electric wires. Properties that are equivalent to conventional electric wires are expected to be attained by overcoming such hurdles as improving and equalizing the electrical conductivity of single fibers and improving the density of yarns. We are working on such development tasks concurrently.

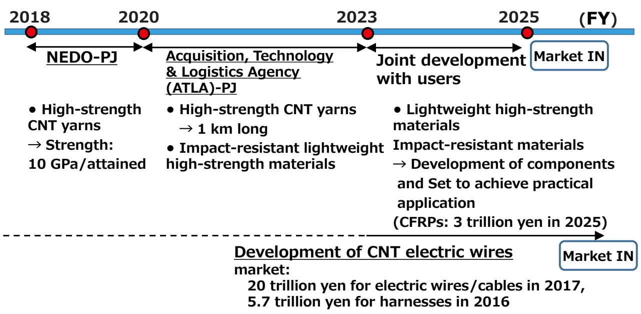

Fig. 10. National Projects and Sumitomo Electric's product development schedule

5. Conclusion

To achieve next-generation electric wires, we have developed a basic technology that can be used for a mass production process by applying a new CNT growth phenomenon. We have succeeded in fabricating CNT yarns of at least one meter. The CNT yarns have attained high strength exceeding that of conventional carbon fibers. We made a breakthrough in the application of CNTs as structural materials. The CNT yarns offer a lot of potential for Sumitomo Electric's structural materials business and for application in automotive parts. We plan to commercialize such yarns as new lightweight high-strength wires. A study on electrical conductivity will also be conducted concurrently to open the way for commercialization of next-generation electric wire materials.

6. Acknowledgments

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Technical Terms

∗1 Thermal CVD (vapor phase synthesis) method: This is a type of Chemical Vapor Deposition (CVD). A raw material gas (a hydrocarbon, such as methane, in the case of CNTs) is decomposed and reacted by the heat of the electric furnace to obtain a desired material.

∗2 Fiber-reinforced plastics (FRPs): Fiber-reinforced plastics are materials whose strength is enhanced by hybridizing plastics with fibers. The strength of composite materials using carbon fibers is particularly high. They are used as structural materials in cars and aircraft.

∗3 Space elevator: A space elevator refers to a transportation system for moving between the Earth's surface and space along a tether (i.e., cable), which extends from a geostationary satellite to the Earth's surface. Such a transportation system would reduce the cost of space transport to one hundredth that of rockets. CNTs are considered to be the only material that can be used for a tether.[11]

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