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(54) **CARBON NANOTUBE AGGREGATE**

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(71) Applicant: **DENSO CORPORATION**, Kariya-city (JP)

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(72) Inventors: **JYUNICHI NARUSE**, Kariya-city (JP); **HAJIME SHINGAI**, Kariya-city (JP); **TAKANORI YOKOI**, Kariya-city (JP); **KATSUMA ISHINO**, Kariya-city (JP)

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(57) **ABSTRACT**

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A carbon nanotube aggregate includes a plurality of carbon nanotubes, a metal compound added to inside and/or outside of each of the carbon nanotubes, and an oxide film that is made of an oxide of the metal compound, and covers an outer periphery of the plurality of carbon nanotubes to define an outer surface of the carbon nanotube aggregate. Since the metal compound is shielded from the atmosphere by the oxide film, separation of the metal compound and reaction of the metal compound with oxygen or water in the atmosphere are suppressed, increasing heat resistance of the carbon nanotube aggregate.

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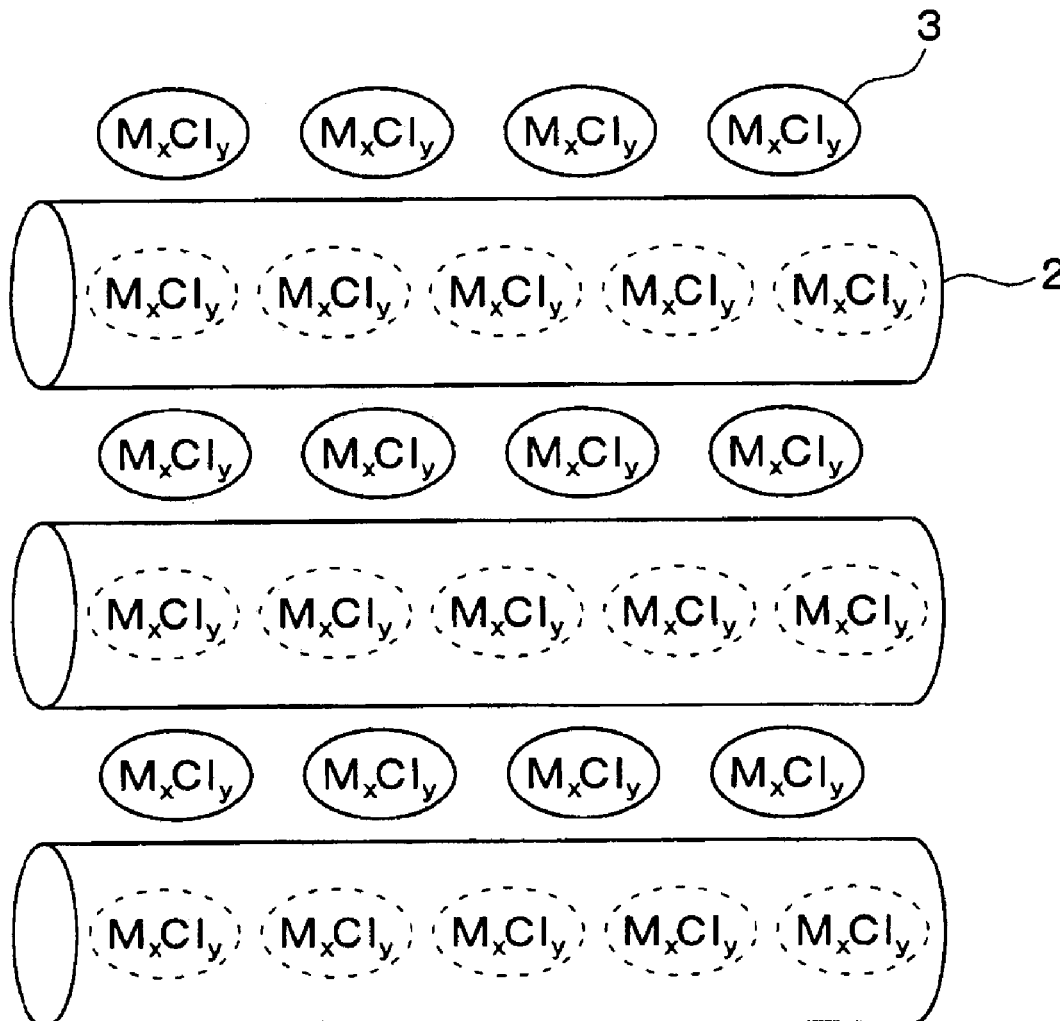


FIG. 1

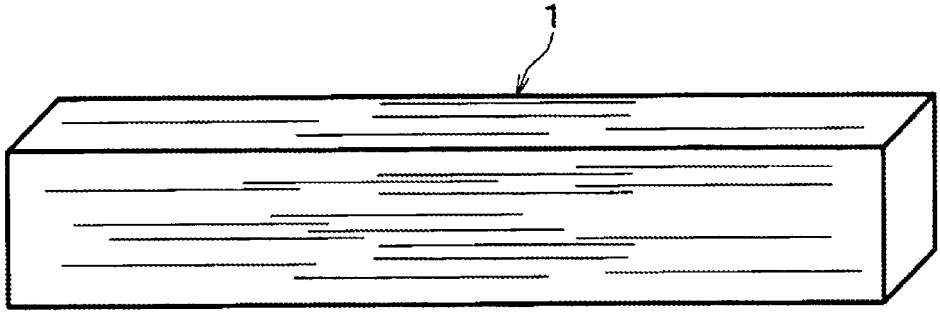


FIG. 2

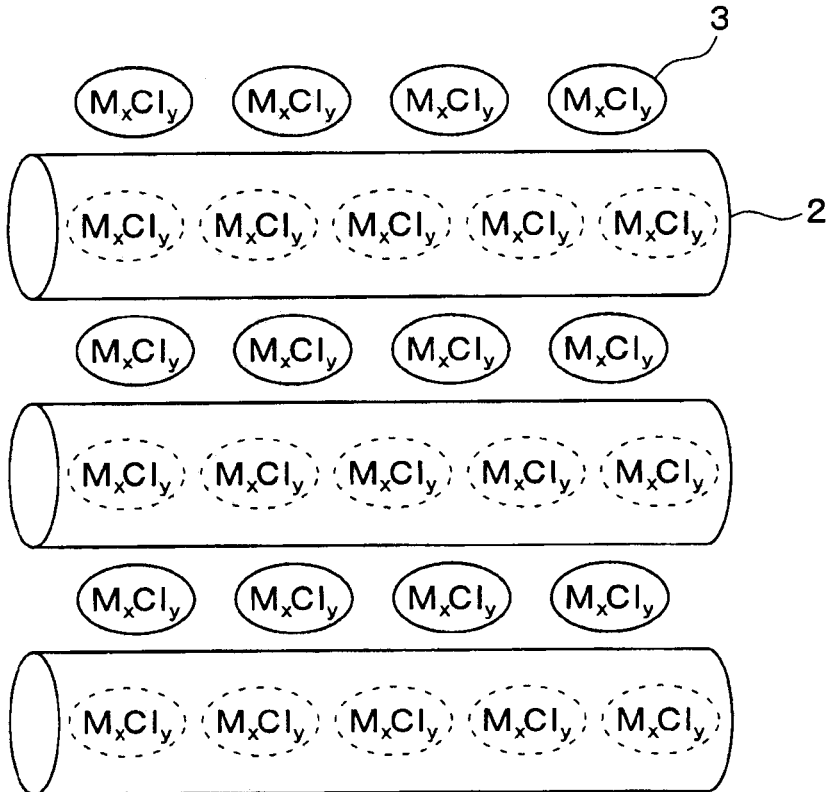


FIG. 3

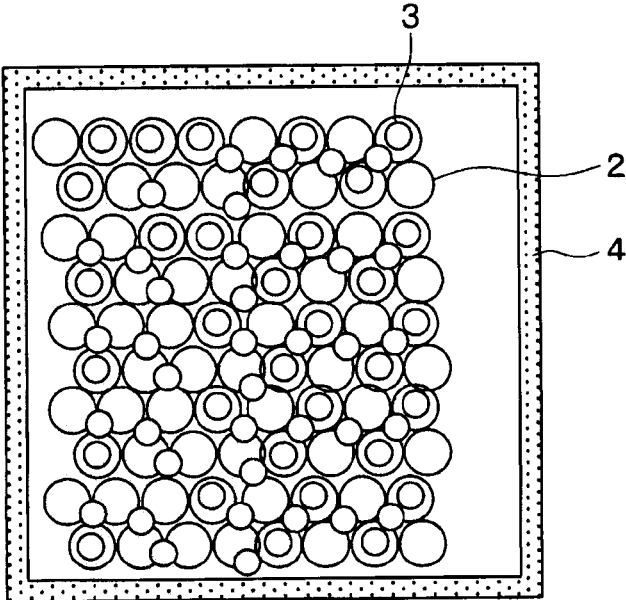


FIG. 4

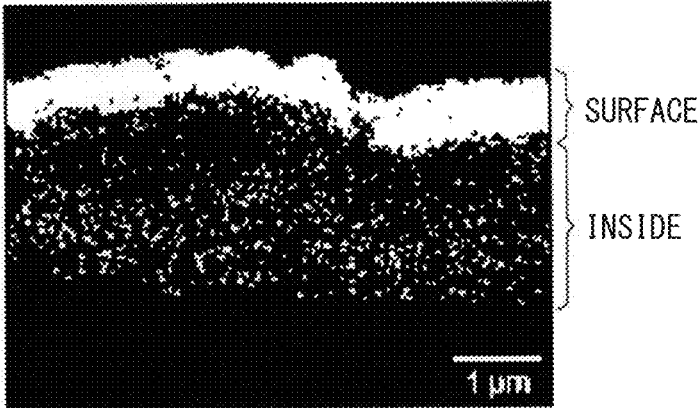


FIG. 5

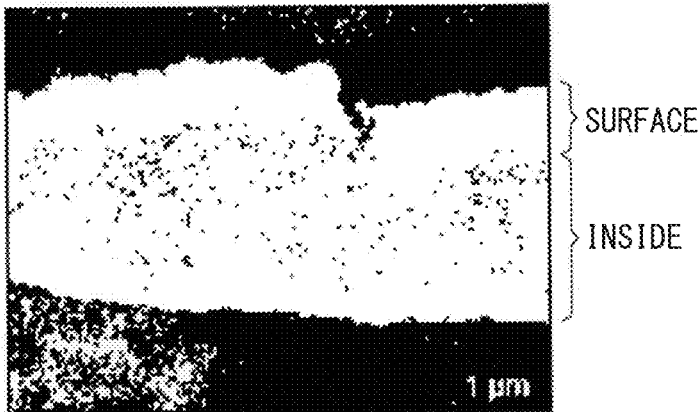


FIG. 6

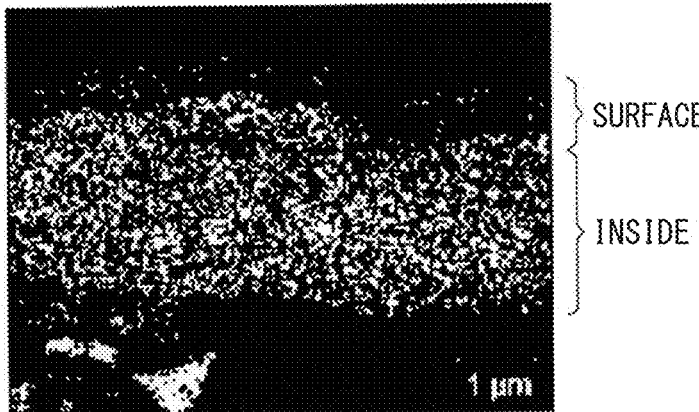


FIG. 7

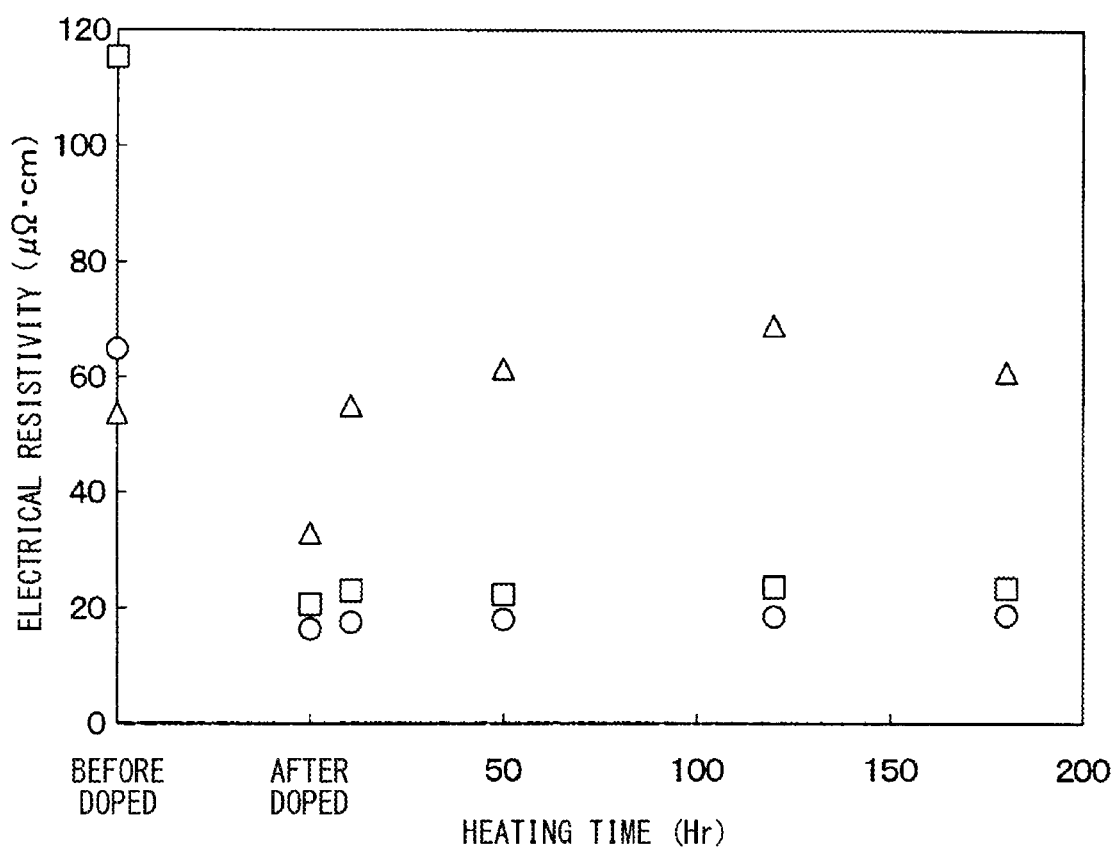


FIG. 8

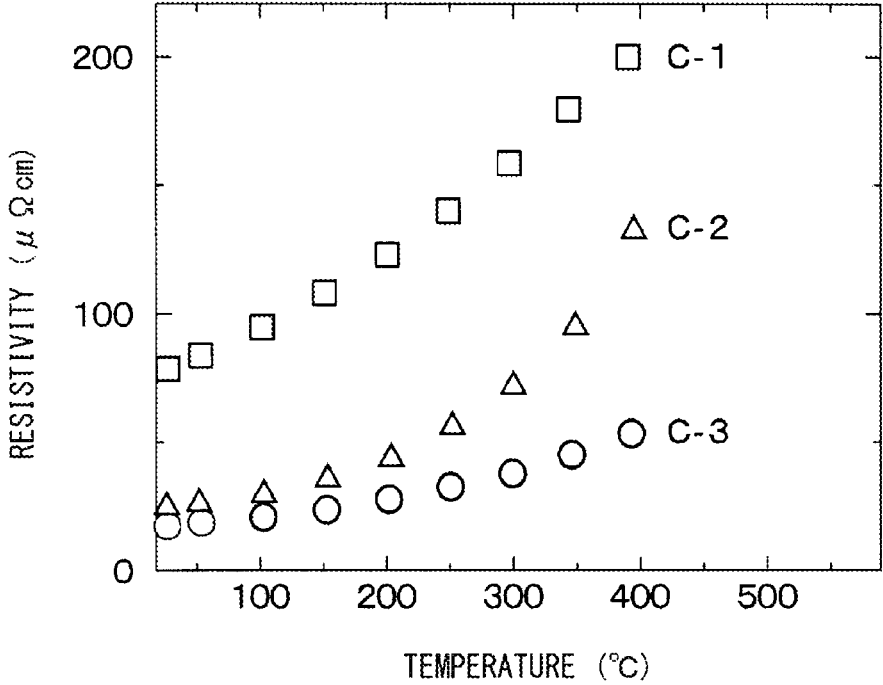


FIG. 9A

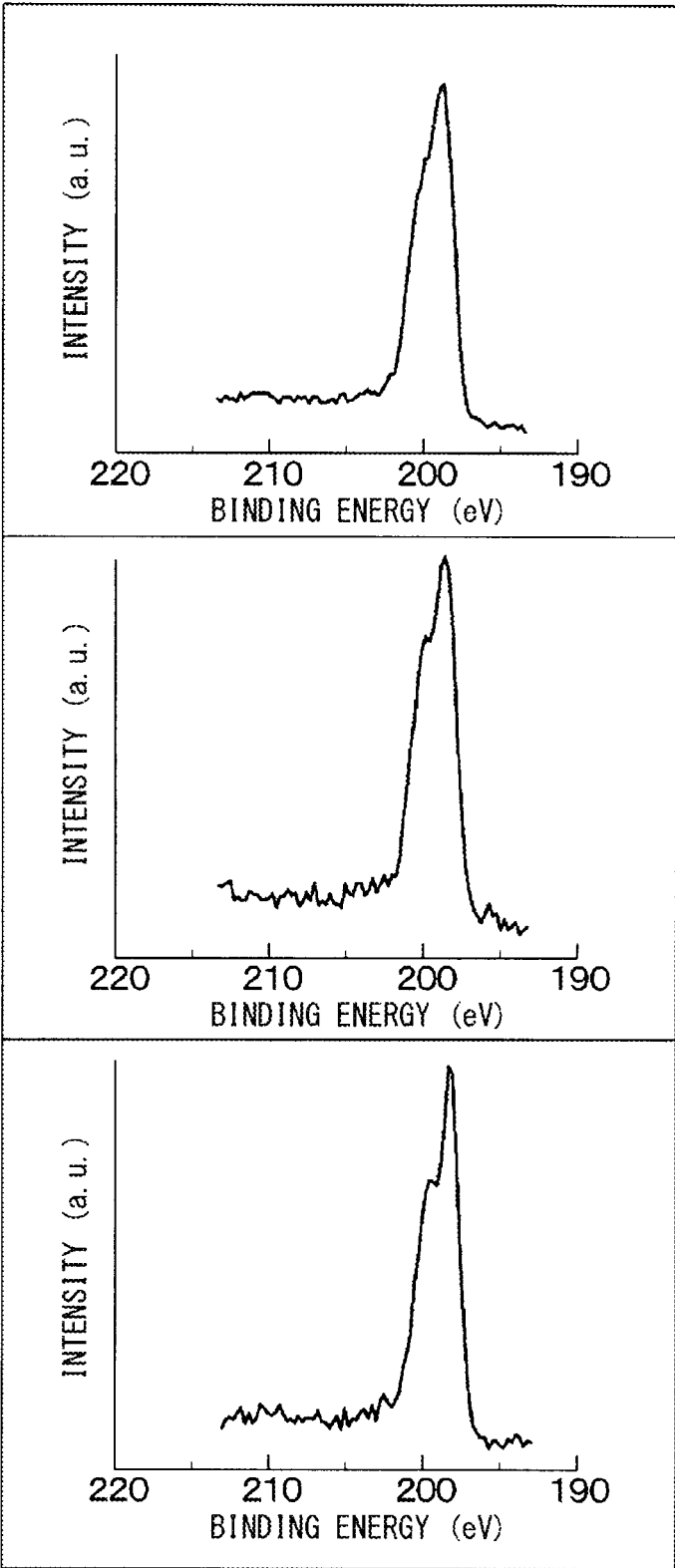


FIG. 9B

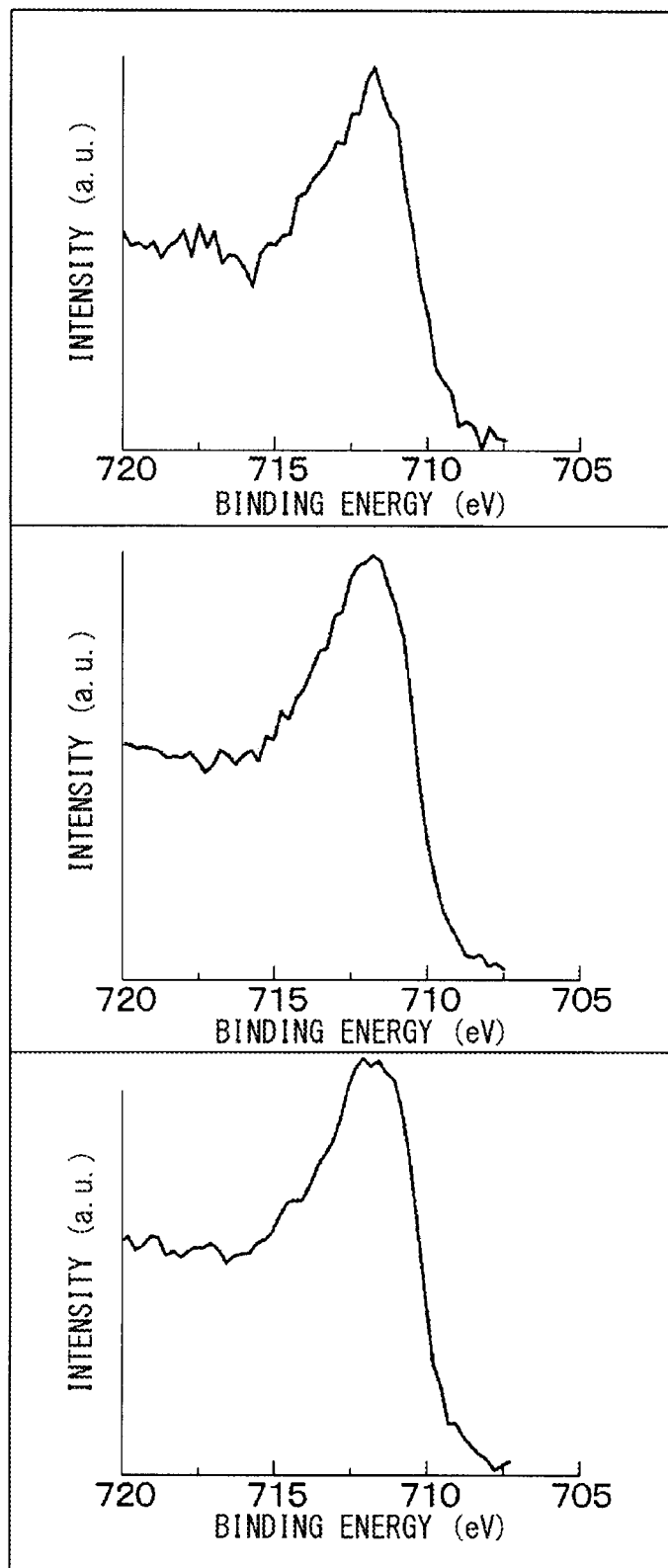
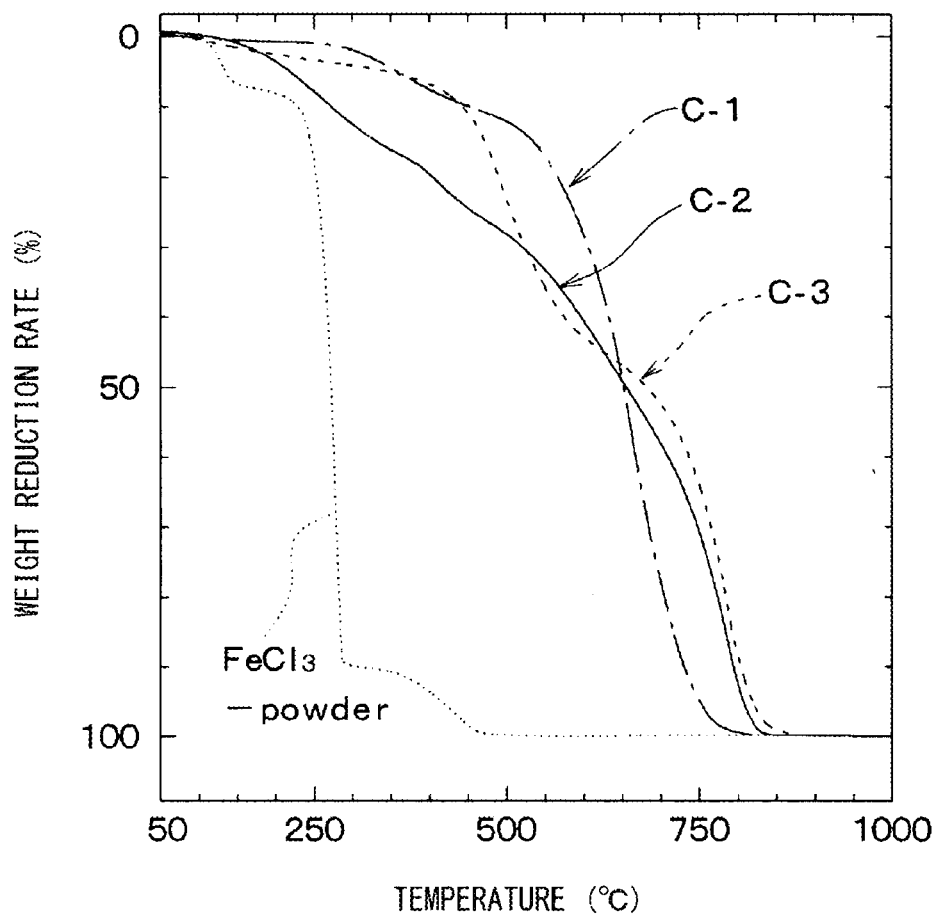


FIG. 10

G BAND PEAK POSITION (cm⁻¹)

SAMPLE	BEFORE HEATING TEST	AFTER HEATING TEST
C-1	1593	—
C-2	1601	1596
C-3	1609	1609

FIG. 11



CARBON NANOTUBE AGGREGATE

CROSS REFERENCE TO RELATED APPLICATION

[0001] The present application claims the benefit of priority from Japanese Patent Application No. 2020-130986 filed on Jul. 31, 2020 and Japanese Patent Application No. 2021-122195 filed on Jul. 27, 2021. The entire disclosures of the above applications are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to an aggregate of carbon nanotubes (hereinafter referred to as CNT).

BACKGROUND

[0003] A CNT aggregate made of a plurality of CNTs is expected to be applied to conductive films and windings. In recent years, there is a demand for lowering electrical resistance due to miniaturization of devices. As a method for lowering the electrical resistance, it is known to conduct a doping treatment to dope CNTs with AuCl_3 , for example, as disclosed in Non-Patent Literature 1.

[0004] Non-Patent Literature 1: Kim et al., Role of Anions in the AuCl_3 -Doping of Carbon Nanotubes, ACS NANO 2011, vol. 5, No. 2, 1236-1242

SUMMARY

[0005] The present disclosure describes a CNT aggregate having a high heat resistance. The CNT aggregate includes a plurality of CNTs, a metal compound added to the inside and/or the outside of the CNTs, and an oxide film made of an oxide of the metal compound and covering an outer periphery of the CNT aggregate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The above and other objects, features and advantages of the present disclosure will become more apparent from the following detailed description made with reference to the accompanying drawings, in which like parts are designated by like reference numbers and in which:

[0007] FIG. 1 is a diagram showing an external view of a CNT aggregate according to a first embodiment;

[0008] FIG. 2 is a diagram showing an internal configuration of the CNT aggregate;

[0009] FIG. 3 is a diagram showing a cross-sectional view of the CNT aggregate;

[0010] FIG. 4 is a photomicrograph showing the content of molybdenum;

[0011] FIG. 5 is a photomicrograph showing the content of oxygen;

[0012] FIG. 6 is a photomicrograph showing the content of chlorine; and

[0013] FIG. 7 is a diagram showing a relationship between heating time and electrical resistance.

[0014] FIG. 8 is a diagram showing the temperature dependence of electrical resistivity of samples C-1 to C-3;

[0015] FIG. 9A is a diagram showing the intensity of an X-ray photoelectron spectroscopic analysis (XPS) spectrum with respect to the binding energy of a Cl 2p region in the sample C-3;

[0016] FIG. 9B is a diagram showing the intensity of the XPS spectrum with respect to the binding energy of a Fe 2p region in the sample C-3;

[0017] FIG. 10 is a diagram showing the measurement results of G band peak positions of the samples C-1 to C-3 in a Raman spectrum; and

[0018] FIG. 11 is a diagram showing the results of thermogravimetric/differential thermal analysis (TG-DTA) in the samples C-1 to C-3 and FeCl_3 powder.

DETAILED DESCRIPTION

[0019] In addition to the lowering of the electrical resistance, CNT aggregates are required to cope with high temperature environments such as for vehicle motors. For example, even if the CNT aggregates are left in the atmosphere of at least 200° C. or higher for 100 hours or longer, it is required that the resistance change is small and the electrical resistance is maintained. However, in a conventional method, such as in a method of Patent Literature 1, although the effect of lowering the electrical resistance is maintained at a temperature of about 100° C., the effect of lowering the electrical resistance is degraded at a temperature of 200° C. or higher. This is considered because of deterioration due to the release of dopant or the reaction with oxygen and water in the atmosphere.

[0020] Further, for n-type CNT materials for thermoelectric materials, a technique of adding an alkali element such as lithium or potassium or a composite of potassium ion and crown ether to the inside of the CNT has been proposed. However, the stability at 200° C. or higher in the atmosphere has not been confirmed. Further, there are few cases in which a p-type dopant, which is more stable in the atmosphere than the n-type dopant, is added to the inside of the CNT. Also, there is no case that exhibits the heat resistance for 100 hours or longer in the atmosphere of 200° C. or higher.

[0021] The present disclosure provides a high heat resistance CNT aggregate.

[0022] According to an aspect of the present disclosure, a CNT aggregate includes a plurality of CNTs, a metal compound added to the inside and/or the outside of the CNTs, and an oxide film made of an oxide of the metal compound and covering an outer periphery of the CNT aggregate.

[0023] In such a configuration, since the metal compound is shielded from the atmosphere by the oxide film covering the surface of the CNT aggregate, the separation of the metal compound and the reaction between the metal compound and oxygen and water in the atmosphere are suppressed. As such, the heat resistance of the CNT aggregate improves.

[0024] The following describes embodiment and examples of the present disclosure with reference to the drawings. In the following embodiment and examples, the same or equivalent parts are denoted by the same reference numerals as each other, and the descriptions there of will not be repeated.

First Embodiment

[0025] A first embodiment will be described. A CNT aggregate 1 of the present embodiment is formed by aggregating a plurality of CNTs 2 to have a rod-shaped or tape-shaped structure, as shown in FIG. 1 and FIG. 2. The CNT aggregate 1 is used, for example, in CNT conductive films, CNT windings for devices, CNT windings for motors, CNT wire harnesses, and the like. The length of one side of

the CNT aggregate **1** is, for example, 10 μm or more. In a case where the CNT aggregate **1** has a quadrangular pillar shape having a quadrangle in a cross-section, the length of one side of the quadrangle is, for example, 10 μm or more. In a case where the CNT aggregate **1** has a columnar shape, the diameter of the CNT aggregate **1** is, for example, 10 μm or more. The density of the CNT aggregate **1** is, for example, 0.8 g/cm^3 or more. The average inner diameter of the plurality of CNTs **2** is, for example, 0.55 nm or more and 1000 nm or less.

[0026] As shown in FIG. 2, in the CNT aggregate **1**, a metal compound **3** such as a metal chloride is added to the inside and the outside of the CNTs **2** in order to reduce the electrical resistance. Here, a case where molybdenum chloride (MoCl_5) is added as the metal compound **3** will be described. In FIG. 2, the CNTs **2** having a columnar shape are shown for the sake of simplicity. Further, the metal compound **3** added to the inside of each of the CNTs **2** is shown by a broken line, and the metal compound **3** added to the outside of the CNT **2** is shown by a solid line.

[0027] As shown in FIG. 3, the surface of the CNT aggregate **1** is covered with an oxide film **4** made of an oxide of the metal compound **3**. In other words, the oxide film **4** forms an outer surface of the CNT aggregate **1**. The oxide film **4** functions to shield the metal compound **3** from the atmosphere, and suppresses the separation of the metal compound **3** and the reaction between the metal compound **3** and oxygen or water in the atmosphere. In a case where MoCl_5 is added as the metal compound **3**, the oxide film **4** is made of molybdenum oxide (MoO_3 , MoO_2) or molybdenum chloride partial oxide ($\text{MoO}_x\text{Cl}_{5-x}$, e.g., $0.1 \leq x < 5$).

[0028] Such a CNT aggregate **1** is produced, for example, by the following procedure. First, a CNT film, which is made of DexMat Inc. (USA), is placed in a vacuum and heated at 500° C. or higher to remove moisture inside a CNT **2**. Next, after mixing the CNT film and MoCl_5 gas in an Ar atmosphere in which O_2 is 1 ppm to 20 ppm, the CNT film is sealed in a container to be shielded from the atmosphere and heated at 260° C. to 350° C. Then, MoCl_5 on the surface of the CNT film is removed by washing with ethanol.

[0029] In this way, MoCl_5 is added as the metal compound **3** inside and/or outside the CNTs **2**, and the CNT aggregate **1** whose surface is covered with an oxide film **4** such as MoO_2 is produced. In this production method, the surface of the CNT aggregate **1** is covered with the oxide film **4**, and openings of the CNT **2** are capped with MoO_2 or the like, which is an oxide of the metal compound **3**.

[0030] FIGS. 4 to 6 are scanning electron micrographs of a cross section of the CNT aggregate **1** produced by the method described above, and show the contents of molybdenum, oxygen, and chlorine in the inside and on the surface of the CNT aggregate **1**. In each of FIGS. 4 to 6, the white area has a higher content of molybdenum, oxygen, and chlorine than the black area. As shown in FIGS. 4 to 6, the surface of the CNT aggregate **1** has higher contents of molybdenum and oxygen and a lower content of chlorine than the inside of the CNT aggregate **1**. Accordingly, it is appreciated that the oxide film **4** mainly composed of molybdenum and oxygen is formed on the surface of the CNT aggregate **1**.

[0031] FIG. 7 is a graph showing the results of examining the heat resistance of the CNT aggregate **1** produced by the method described above. In FIG. 7, the horizontal axis represents a heating time when a heating test is performed at

230° C. in the atmosphere, and the vertical axis represents an electrical resistivity measured by a four-terminal measurement method at room temperature after removing the CNT aggregate from a heating device. In FIG. 7, white circles indicate the electrical resistivity of the CNT aggregate **1** in which a molybdenum oxide film thicker than 1 nm and thinner than 10 nm is formed on the surface. White squares indicate the electrical resistivity of the CNT aggregate **1** in which a molybdenum oxide film having a thickness of 10 nm is formed on the surface. Further, the white triangles indicate the electrical resistivity of a CNT aggregate to which AuCl_3 is added and in which no oxide film is formed on the surface.

[0032] As shown in FIG. 7, when the CNT aggregate in which the oxide film is not formed on the surface is heated at 230° C., the electrical resistance increases in a short time to the level of that before the addition of AuCl_3 . On the other hand, in the CNT aggregate **1** in which the oxide film **4** is formed on the surface, the electrical resistance does not increase significantly even after heated for a long time and is kept small.

[0033] In the present embodiment, as described above, the electrical resistance of the CNT aggregate **1** is lowered as the metal compound **3** is added to the inside and outside of the CNTs **2**. In addition, since the surface of the CNT aggregate **1** is covered with the oxide film **4** made of the oxide of the metal compound **3**, the metal compound **3** is shielded from the air. As a result, the heat resistance is improved as compared with the conventional aggregate. The heat resistance of 200° C. or higher can be achieved.

[0034] Further, in a case where openings of the CNTs **2** are capped with the oxide of the metal compound **3**, the metal compound **3** inside the CNTs **2** is shielded from the air. In such a case, the heat resistance is further improved.

[0035] The improvement of the heat resistance can also be confirmed in a doping test in which the CNT film is doped with FeCl_3 . In this case, as the CNT film, GALVORN CNT TAPE manufactured by DexMat INC. (USA) was used. The initial resistance of the CNT film was $33.8 \pm 6.9 \mu\Omega\text{cm}$. When this CNT film was subjected to a heat treatment at 350° C. for 1 hour in the air, the initial resistance after the heat treatment was $61.2 \pm 8.4 \mu\Omega\text{cm}$. Further, the following three types of samples, C-1, C-2, and C-3, were prepared, in which the sample C-1 was a CNT film after the heat treatment and the samples C-2 and C-3 were the CNT films further subjected to a doping treatment after the heat treatment. Specifically, the sample C-1 was a CNT film subjected to the heat treatment only, the sample C-2 was a CNT film doped with IBr after the heat treatment, and the sample C-3 was a CNT film doped with FeCl_3 after the heat treatment. In the sample C-3, 99.9% pure anhydrous FeCl_3 made by Sigma Aldrich was used without purification and added as a dopant. In the sample C-2, 98% pure IBr made by Sigma Aldrich was used without purification and added as a dopant. In the doping treatment, the CNT film and the dopant were both placed in a closed container filled with an inert gas, and the treatment was carried out at 270° C. for 24 hours. After the doping treatment, the CNT film was washed with ethanol several times to remove excess dopant adsorbed on its surface.

[0036] Then, in order to investigate the temperature dependence on the electrical resistivity, the electrical resistivity of each of the samples C-1 to C-3 under an inert gas atmosphere were measured. The electrical resistivity was measured at a rate in which the temperature was increased

by 25° C. per minute. FIG. 8 shows the measurement results. As shown FIG. 8, the electrical resistivity of all three types of the samples C-1 to C-3 was increased by the heating from the room temperature. In particular, the rate of increase in the electrical resistivity of the sample C-3 with the increase in the temperature was lower than that of the sample C-2, and the rate of change was also small.

[0037] In addition, the thermal stability was confirmed by analyzing the characteristics of the doped CNT film. In the analysis, a Raman spectroscopic analysis (hereinafter referred to as Raman), an X-ray photoelectron spectroscopic analysis (hereinafter referred to as XPS) and a thermogravimetric/differential thermal analysis (hereinafter referred to as TG-DTA) were performed. In the Raman, an excitation wavelength of 532 nm was used, and a confocal Raman microscope, InVia Qontor made by Renishaw (UK) was used. In the XPS, PHI 5000 VersaProbe II made by ULVAC-PHI, Inc. (JAPAN) was used, X-rays were focused on a spot size having a diameter of 200 μm on the sample under 50 W. As an X-ray source, Al-Kα ray (hν=1486.6 eV) was used. In the TG-DTA performed for the evaluation of the thermal stability of each sample, TG-DTA 6300 made by Hitachi High-Technologies Corporation (JAPAN) was used. In the TG-DTA, the measurement temperature range was 40° C. to 1000° C., and under the condition that the scanning speed was increased by +10.0° C. per minute, the air was introduced at 100 mL per minute using an alumina pan.

[0038] In the XPS measurement, in order to detect Fe and Cl inside the CNT doped with FeCl₃, attention was paid to the peaks in the Fe 2p region near 712 eV and the Cl 2p region near 198 eV. FIGS. 9A and 9B show the relationship between the binding energy (eV) and the intensity (a.u.) of the XPS spectrum, respectively, in the Cl 2p region near 198 eV of the sample C-3 and the Fe 2p region near 712 eV of the sample C-3. In each of FIG. 9A and 9B, the top spectrum shows the result before heating, the middle spectrum shows the result after heating for 50 hours, and the bottom spectrum shows the result after heating for 120 hours.

[0039] As can be seen from FIGS. 9A and 9B, in the XPS spectrum of the sample C-3, peak disappearance and peak shape change were not observed in the region of interest before the heating and after the heating. Therefore, it can be said that FeCl₃ is retained in the CNT even at a high temperature of about 220° C., which is assumed when the CNT aggregate 1 is applied to a motor or the like.

[0040] Also, the shift of the G band peak position in the Raman spectrum reflects the state of p-type doping in the CNT. FIG. 10 shows the results of measurement of the G band peak position of the Raman spectrum using excitation light having an excitation wavelength of 532 nm in the samples C-1 to C-3. A high-temperature standing test was performed on each sample, and the G band peak positions before and after the heat treatment in the high-temperature leaving test were measured. However, the sample C-1 was an undoped sample and was considered to have no change in the G band peak positions before and after the heat treatment. Therefore, only the measurement result before the heat treatment is shown for the sample C-1.

[0041] In the results of the high temperature standing test, the G band peak positions of the samples C-2 and C-3 before the heat treatment were 1601 cm⁻¹ and 1609 cm⁻¹, respectively. Thus, as compared with the peak position 1593 cm⁻¹ of the sample C-1, the peak shifts of the sample C-2 and C-3 are large, in proportion to the change in resistivity. On the

other hand, in the results of the samples C-2 and C-3 after the heat treatment, the G band peak position of the sample C-2 was 1596 m⁻¹, whereas the G band position of the sample C-3 did not change before and after the heat treatment. This suggests that, in the sample C-3, the p-type doping state is retained before and after the heat treatment.

[0042] In the TG-DTA, the analysis was performed on the samples C-1 to C-3 and FeCl₃ powders. As a result, FeCl₃ showed different thermal stability with and without doping, as shown in FIG. 11. That is, it was confirmed that the thermogravimetric analysis (TG) of the FeCl₃ powder alone shows a weight reduction from around 200° C., while the sample C-3 shows a rapid weight reduction from around 500° C. and from around 700° C. In the sample C-3, since the rapid weight reduction and the gradient in the temperature range around 500° C. and around 700° C. were substantially the same as those of the sample C-1, it can be inferred that the weight reduction is due to the weight reduction of the CNT itself. In the FeCl₃ powder alone, it can be inferred that the weight reduction is due to the weight reduction of the FeCl₃ itself. Accordingly, it is considered that FeCl₃ contained in the CNT and the CNT are thermally stable, relative to the simple substance. This feature was also confirmed in the sample C-2, and it can be said that it supports the result of improvement in thermal stability due to inclusion of another substance.

Other Embodiments

[0043] The present disclosure is not limited to the above embodiment, and can be appropriately modified in various ways.

[0044] For example, in the embodiment described above, MoCl₅ is added to the CNT aggregate 1 as the metal compound 3. Alternatively, another metal chloride may be added, or a metal compound other than the metal chloride may be added. For example, FeCl₃ may be added. Further, the metal compound 3 may be added only to the inside of the CNTs 2 or may be added only to the outside of the CNTs 2.

[0045] While only the selected exemplary embodiment and examples have been chosen to illustrate the present disclosure, it will be apparent to those skilled in the art from this disclosure that various changes and modifications can be made therein without departing from the scope of the disclosure as defined in the appended claims. Furthermore, the foregoing description of the exemplary embodiment and examples according to the present disclosure is provided for illustration only, and not for the purpose of limiting the disclosure as defined by the appended claims and their equivalents.

What is claimed is:

1. A carbon nanotube aggregate comprising:
 - a plurality of carbon nanotubes;
 - a metal compound added to inside and/or outside of each of the carbon nanotubes; and
 - an oxide film made of an oxide of the metal compound, and covering an outer periphery of the plurality of carbon nanotubes to define an outer surface of the carbon nanotube aggregate.
2. The carbon nanotube aggregate according to claim 1, wherein the metal compound is a metal chloride.

3. The carbon nanotube aggregate according to claim 2, wherein the metal compound is molybdenum chloride, and wherein the oxide is molybdenum oxide or a partial oxide of molybdenum chloride.

4. The carbon nanotube aggregate according to claim 1, wherein the carbon nanotube aggregate has a quadrangular pillar shape in which a length of one side is 10 μm or more, or a columnar shape having a diameter of 10 μm or more.

5. The carbon nanotube aggregate according to claim 1, wherein a density of the plurality of carbon nanotubes is 0.8 g/cm^3 or more.

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