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(54) **Carbon nanotubes fiber having low resistivity**

(57) Carbon nanotubes (CNT) fibers having a resistivity lower than $120 \mu\Omega \cdot \text{cm}$ are prepared by a process comprising the steps of supplying a spin-dope comprising carbon nanotubes to a spinneret, extruding the spin-dope through at least one spinning hole in the spinneret to form spun carbon nanotubes fibers, coagulating the spun carbon nanotubes fibers in a coagulation medium to form coagulated carbon nanotubes fibers, wherein the carbon

nanotubes fibers are drawn at a draw ratio of at least 0.8, preferably higher than 1.0, and wherein the carbon nanotubes have a length of at least $0,5 \mu\text{m}$, preferably of at least $2 \mu\text{m}$. The carbon nanotubes preferably have a G/D ratio of at least 10. In another aspect, carbon nanotubes (CNT) fibers are disclosed having a modulus of at least 150 GPa, preferably at least 200 GPa.

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Description

[0001] The invention pertains to carbon nanotubes fibers having low resistivity and/or high modulus and to composite articles comprising carbon nanotubes fibers having low resistivity and/or high modulus. The invention also pertains to a process for manufacturing carbon nanotubes fibers having low resistivity and/or high modulus.

[0002] State of the art methods to produce carbon nanotube fibers of low resistivity are based on dry processing. For example, Nanocomp Technologies use a process based on twisting carbon nanotube aero gels into fibers. Low resistivity is achieved by doping these fibers. Values of $50 \mu\Omega\cdot\text{cm}$ have been achieved by doping. Production of carbon nanotubes fibers by dry processing is however very laborious and doping requires an additional processing step.

[0003] An alternative to dry processing of nanotubes is wet processing. US 7,125,502 B2 discloses fibers of single wall carbon nanotubes spun through dies having diameters of $500 \mu\text{m}$, $250 \mu\text{m}$ and $125 \mu\text{m}$. Drawing was not applied during spinning of the carbon nanotubes (CNT) fibers. Resistivity of the CNT fibers was $300 \mu\Omega\cdot\text{cm}$ and higher.

[0004] WO 2009/058855 A2 discloses carbon nanotubes fibers spun through orifices having a diameter of 50 to $500 \mu\text{m}$. CNT fibers having resistivity of $120 \mu\Omega\cdot\text{cm}$ and higher have been produced by the method of WO2009/058855.

[0005] Fibers having low resistivity can advantageously be used in many applications such as for example light weight cables for electrical power transmission and for data transmission.

[0006] It is an object of the present invention to provide carbon nanotubes fibers having low resistivity and/or high modulus.

[0007] The spinning process according to the invention enables manufacturing of CNT fibers having resistivity below $120 \mu\Omega\cdot\text{cm}$, lower than state-of-the art wet spinning processes. In a preferred embodiment, the resistivity of the CNT fibers is below $50 \mu\Omega\cdot\text{cm}$, which is lower than reported for nanotube fibers from any known production process. At the same time, the CNT fibers can have high modulus.

[0008] For a person skilled in the art it is clear that a batch of carbon nanotubes will have a distribution in diameter, length and chirality. Carbon nanotubes as used in the invention are to be understood to mean any type of carbon nanotubes, such as single wall carbon nanotubes (SWNT), double wall carbon nanotubes (DWNT) or multiwall carbon nanotubes (MWNT) and mixtures thereof, having an average length at least 10 times its average outer diameter, preferably at least 100 times its outer diameter, most preferably at least 1000 times its outer diameter. The carbon nanotubes may be open ended carbon nanotubes or closed carbon nanotubes.

[0009] The term carbon nanotubes fiber as used in this invention is to be understood to include the final product

and any intermediate of the spun carbon nanotubes. For example, it encompasses the liquid stream of spin-dope spun out of the spinning hole(s) of the spinneret, the partly and fully coagulated fibers as present in the coagulation medium, the drawn fibers, and it encompasses also the stripped, neutralized, washed and/or heat treated final fiber product. The term fiber is to be understood to include filaments, yarns, ribbons and tapes.

[0010] Carbon nanotubes fibers having low resistivity have a high electrical conductivity. Conductivity is to be understood to mean the inverse of the resistivity. Carbon nanotubes fibers according to the invention may also exhibit a high thermal conductivity.

[0011] The process according to the present invention comprises the steps of supplying a spin-dope comprising carbon nanotubes (CNT) to a spinneret, extruding the spin-dope through at least one spinning hole in the spinneret to form spun CNT fiber(s), coagulating the spun CNT fiber(s) in a coagulation medium to form coagulated CNT fibers wherein the fiber(s) are drawn at a draw ratio of at least 0.8 and wherein the carbon nanotubes have an average length of at least $0.5 \mu\text{m}$.

[0012] Preferably, the carbon nanotubes have an average length of at least $1 \mu\text{m}$, more preferably at least $2 \mu\text{m}$, even more preferably at least $5 \mu\text{m}$, even more preferably at least $15 \mu\text{m}$, most preferably at least $20 \mu\text{m}$.

[0013] When the carbon nanotubes have an average length of at least $0.5 \mu\text{m}$, CNT fibers can be prepared having low resistivity and/or high modulus. However, nanotubes having a length in the range of 10 to $15 \mu\text{m}$ are potentially hazardous for humans (particularly in case no precautionary measures have been taken) and therefore nanotubes having a length of at least $15 \mu\text{m}$ are especially preferred.

[0014] Without being bound to theory, it is believed that the quality of a CNT fiber having low resistivity is determined by the quality of the carbon nanotubes and the length of the carbon nanotube ropes in the CNT fibers.

[0015] A carbon nanotube rope is to be understood to mean an elongated assembly of predominantly parallel carbon nanotubes, 30 to 200 nm in diameter.

[0016] The length of the nanotubes ropes in the CNT fibers should preferably be in the range of $1 \mu\text{m}$ to 5 mm . It is believed that the length of the nanotubes ropes in the CNT fibers is influenced by the concentration of carbon nanotubes in the spin-dope, by the average length of the carbon nanotubes, by the size of the spinning holes, by the viscosity of the spin-dope and/or by the draw ratio applied to the spun CNT fibers.

[0017] Preferably, the carbon nanotubes have a high quality as defined by the G/D ratio. The high quality is needed to be able to disperse the nanotubes. Nanotubes can be dissolved in acids if the G/D ratio is above 4. Without being bound to any theory, it is believed that using carbon nanotubes having a higher G/D ratio than 4 decreases the resistivity of resulting CNT fibers. For the present the G/D ratio is preferably higher than 10. The G/D ratio of the carbon nanotubes is determined

using Raman spectroscopy at a wavelength of 514 nm.

[0018] The carbon nanotubes may contain up to about 30 wt.% impurities, such as for example amorphous carbon and catalyst residues.

[0019] The spin-dope may comprise metallic carbon nanotubes and/or semi-conducting carbon nanotubes.

[0020] The spin-dope can be formed by dissolving carbon nanotubes in a suitable solvent, preferably a super acid. Additionally, the spin-dope may comprise polymers, coagulants, surfactants, salts, nanoparticles, dyes or materials that can improve conductivity. Preferably, the carbon nanotubes are purified and/or dried before dissolving the carbon nanotubes in the solvent.

[0021] The spin-dope preferably comprises 0.2 wt.% to 25 wt.% carbon nanotubes, based on the total weight of the spin-dope, preferably 0.5 wt.% to 20 wt.%, more preferably 1 wt.% to 15 wt.%.

[0022] The spin-dope comprising carbon nanotubes is supplied to a spinneret and extruded through at least one spinning hole to obtain spun CNT fiber(s). The spinneret may contain any number of spinning holes, ranging from one spinning hole to manufacture CNT monofilament up to several thousands to produce multifilament CNT yarns.

[0023] In an embodiment of the process to obtain CNT fibers having low resistivity the spinning hole(s) in the spinneret are circular and have a diameter in the range of 10 to 1000 μm , more preferably in the range of 25 to 500 μm , even more preferably in the range of 40 to 250 μm .

[0024] In an alternative embodiment, the spinning holes may have a non-circular cross section, such as for example rectangular, having a major dimension defining the largest distance between two opposing sides of the cross section and a minor dimension defining smallest distance between two opposing sides of the cross section. The minor dimension of the non-circular cross section is preferably in the range of 10 to 1000 μm , more preferably in the range of 25 to 500 μm , even more preferably in the range of 40 to 250 μm .

[0025] The entrance opening of the spinning hole(s) may be tapered.

[0026] The extruded CNT fiber(s), also called spun CNT fiber(s), may be spun directly into the coagulation medium, or guided into the coagulation medium via an air gap. The coagulation medium may be contained in a coagulation bath, or may be supplied in a coagulation curtain. The coagulation medium in the coagulation bath may be stagnant or there may be a flow of coagulation medium inside or through the coagulation bath.

[0027] The spun CNT fibers may enter the coagulation medium directly to coagulate the CNT fibers to increase the strength of the CNT fibers to ensure that the CNT fibers are strong enough to support their own weight. The speed of the CNT fiber(s) in the coagulation medium is in general established by the speed of a speed-driven godet or winder after the CNT fibers have been coagulated and optionally neutralized and/or washed.

[0028] In an air gap the spun CNT fiber(s) can be drawn to increase the orientation in the CNT fiber(s) and the air gap avoids direct contact between spinneret and coagulation medium. The speed of the CNT fiber(s) and thus the draw ratio in the air gap is in general established by the speed of a speed-driven godet or winder after the CNT fibers have been coagulated and optionally neutralized and/or washed.

[0029] Preferably, the extruded fibers directly enter into the coagulation medium.

[0030] The coagulation speed of CNT fibers may be influenced by flow of the coagulation medium. In the processes according to the invention the coagulation medium may flow in the same direction as the CNT fibers. The flow velocity of coagulation medium can be selected to be lower, equal to or higher than the speed of the CNT fibers.

[0031] The extruded CNT fibers may be spun horizontally, vertically or even under an angle to the vertical direction.

[0032] In an embodiment, the extruded CNT fibers are spun horizontally. Horizontal spinning can for example be advantageous to keep the coagulation bath shallow. Carbon nanotubes fibers may be retrieved relatively easy from the shallow coagulation bath at start up of the process or when breakage of the CNT fiber occurs.

[0033] The extruded CNT fibers may be spun directly into the coagulation bath in a horizontal direction. The extruded CNT fibers are only limitedly influenced by gravity forces and are supported by the liquid coagulation medium and will therefore not break up into smaller pieces under their own weight.

[0034] In an embodiment the extruded CNT fibers are spun directly into a coagulation bath in the shape of a tube wherein coagulation medium may flow in the same direction as the CNT fibers. The flow velocity of the coagulation medium is determined by the fluid flow supplied to the tube and the diameter of the transport tube and can be set to any desired value relative to the speed of the CNT fibers.

[0035] Alternatively, the tube may be submerged in coagulation medium inside a larger coagulation bath. Without CNT fibers, the flow velocity of the coagulation medium inside the tube is determined by the height difference between the liquid level of the coagulation bath and the outlet of the transport tube.

[0036] The extruded CNT fibers may be spun vertically through an air gap before entering a coagulation bath containing coagulation medium or may be spun vertically directly in a coagulation bath containing coagulation medium.

[0037] Alternatively, the extruded CNT fibers may be spun vertically into a curtain of coagulation medium, with or without air-gap. The curtain of coagulation medium can easily be formed by using an overflow system.

[0038] The extruded CNT fibers may be spun directly into the coagulation medium vertically upward or under an angle between the horizontal and the vertically upward

direction, i.e. in a direction against gravity. Extruding CNT fibers in a direction against gravity is especially preferred when the density of the spun CNT fibers is lower than the density of the coagulation medium. At start-up of the process the extruded CNT fibers will float towards the top end of the coagulation bath where the CNT fibers can be picked up from the surface.

[0039] The coagulation bath containing the coagulation medium may be in the shape of a tube wherein coagulation medium may flow from the bottom to the top of the tube. The flow velocity of the coagulation medium is determined by the fluid flow supplied to the tube and the diameter of the transport tube and can be set to any desired value relative to the speed of the CNT fibers.

[0040] Suitable coagulation media are for example sulphuric acid, PEG-200, dichloromethane, trichloromethane, tetrachloromethane, ether, water, alcohols, such as methanol, ethanol and propanol, acetone, N-methyl pyrrolidone (NMP), dimethylsulfoxide (DMSO), sulfolane. The coagulant can contain dissolved material such as surfactant or polymer such as polyvinylalcohol (PVA). It is also possible to add agents to the coagulation medium that can be entrapped in the fiber to enhance its properties, such as but not limited to polymers, surfactants, salts, nanoparticles, dyes and materials that can improve conductivity such as iodine. Preferably, the coagulation medium is water or acetone.

[0041] To obtain CNT fiber having low resistivity and/or high modulus, drawing has to be applied to the spun CNT fiber at a draw ratio of at least 0.8, preferably at least 1.0, more preferably at least 1.1, more preferably at least 1.2, even more preferably higher than 5, most preferably higher than 10.

[0042] High draw ratio can also be used to tune the diameter of the resulting fibers.

[0043] Drawing of the spun CNT fiber(s) can be applied in a one-step process, wherein the spin-dope is extruded through the spinning hole(s), the spun CNT fiber(s) are drawn and optionally coagulated, stripped, neutralized and/or washed, and wound in one continuous process.

[0044] Alternatively, drawn CNT fibers can be prepared in two-step process. In the first processing step the spin-dope is extruded through the spinning hole(s), the spun CNT fiber(s) are optionally coagulated, stripped, neutralized and/or washed, and wound. Subsequently, the spun and optionally coagulated, stripped, neutralized and/or washed CNT fibers are unwound and drawn in a separate drawing process.

[0045] Drawing of the CNT fibers may preferably be executed in a liquid swelling medium, which causes swelling of the CNT fibers. It is believed that swelling of the CNT fibers decreases bonding between neighboring carbon nanotubes in the CNT fiber, which enables improved alignment of carbon nanotubes during drawing of the CNT fibers. In the second processing the fibers can also optionally be coagulated, stripped, neutralized and/or washed before being wound.

[0046] Suitable swelling media are for example strong

acids, such as chlorosulfonic acid, oleum, sulfuric acid, triflic acid, mixtures thereof and dilution thereof. Preferably, the swelling medium is sulfuric acid.

[0047] In a one-step process, the draw ratio is to be understood to mean the ratio of the winding speed of the CNT fiber(s) over the superficial velocity of the spin-dope in the spinning hole(s). The superficial velocity can be calculated as the volume of spin-dope extruded through the spinning hole(s) divided by the cross sectional area of the spinning hole(s). In the alternative that the CNT is drawn in a separate processing step in a two-step process, the draw ratio is to be understood to mean the ratio of the winding speed of the CNT fiber(s) after drawing over the unwinding speed.

[0048] The combination of carbon nanotubes having a G/D ratio of at least 4, preferably at least 10, and a length of at least 0.5 μm , and a draw ratio of at least 0.8 applied to the spun CNT fiber is especially advantageously in obtaining CNT fibers having low resistivity.

[0049] To obtain low resistivity CNT fiber it is advantageous that the spin-dope comprising carbon nanotubes has been mixed thoroughly to obtain a homogeneous spin-dope. Preferably, the spin-dope is obtained by mixing carbon nanotubes with a solvent, preferably a super-acid, to dissolve the carbon nanotubes in the solvent.

[0050] Dissolving carbon nanotubes in a solvent means that each single carbon nanotube is fully surrounded by the solvent or that the carbon nanotubes are present in conglomerates of two, three or more carbon nanotubes, up to about 50 nanotubes, whereby the conglomerates are fully surrounded by the solvent and the carbon nanotubes in the conglomerates are adjacent or partly adjacent to one another without solvent being present between the adjacent carbon nanotubes.

[0051] Preferably, the carbon nanotubes are mixed with a super-acid, preferably chlorosulfonic acid.

[0052] Preferably, the spin-dope comprising carbon nanotubes passes through one or more filters before being supplied to the spinning hole(s) to further improve the quality of the spin-dope.

[0053] To obtain CNT fiber having low resistivity it is further advantageous that the spin-dope comprises double wall carbon nanotubes (DWNT) having a length of at least 0.5 μm , preferably at least 1 μm , more preferably at least 2 μm , even more preferably at least 5 μm , even more preferably at least 15 μm , even more preferably at least 20 μm , most preferably at least 100 μm .

[0054] In another preferred embodiment the spin-dope comprises single wall carbon nanotubes (SWNT) having a length of at least 0.5 μm , preferably at least 1 μm , more preferably at least 2 μm , even more preferably at least 5 μm , even more preferably at least 20 μm , most preferably at least 100 μm .

[0055] In yet another preferred embodiment the spin-dope comprises mixtures of carbon nanotubes with different amounts of walls, having a length of at least 0.5 μm , preferably at least 1 μm , more preferably at least 2 μm , even more preferably at least 5 μm , even more pref-

erably at least 20 μm , most preferably at least 100 μm .

[0056] The spun and coagulated CNT fiber can be collected on a winder. The inventive process makes it possible to manufacture CNT fibers at industrial winding speeds. The winding preferably is at least 0.1 m/min, more preferably 1 m/min, even more preferably at least 5 m/min, even more preferably at least 50 m/min, most preferably at least 100 m/min.

[0057] The spun and coagulated CNT fiber can optionally be neutralized and/or washed, preferably with water, and subsequently dried.

[0058] The winder may be located inside the coagulation bath to wash the coagulated CNT fiber while being wound on a bobbin, which is especially useful when the coagulation medium used to coagulate the spun fiber(s) is also suitable to wash the CNT fibers, for example when the coagulation medium is water. The winder may be submersed fully or only partially in the coagulation medium. Preferably, the bobbin collecting the CNT fiber(s) is submersed only partially in the coagulation medium.

[0059] Drying can be performed by any known drying technique, such as for example hot air drying, infra red heating, vacuum drying, etc.

[0060] After drying, resistivity may be further improved by doping the fiber with substances such as but not limited to iodine, potassium, acids or salts.

[0061] Carbon nanotubes (CNT) fiber according to the invention have a resistivity less than 120 $\mu\Omega\cdot\text{cm}$. Preferably, the CNT fiber has a resistivity less than 100 $\mu\Omega\cdot\text{cm}$, more preferably less than 50 $\mu\Omega\cdot\text{cm}$, even more preferably less than 20 $\mu\Omega\cdot\text{cm}$, most preferably less than 10 $\mu\Omega\cdot\text{cm}$.

[0062] The wet spinning process according to the invention enables manufacturing of CNT fibers having resistivity below 120 $\mu\Omega\cdot\text{cm}$, lower than state-of-the art wet spinning processes. In a preferred embodiment, the resistivity of the CNT fibers is below 50 $\mu\Omega\cdot\text{cm}$, which is lower than reported for nanotube fibers from any known production process. At the same time, the CNT fibers can have high modulus.

[0063] Resistivity has been determined using a 2 point probe method. A fiber is glued to a microscope glass slide with silver paste at three positions. The resistance between points 1 and 2, points 2 and 3 and points 1 and 3 is measured. This resistance is plotted vs. the length between the silver paste spots. The slope of the resistance vs. length is multiplied by the surface area of the fiber to obtain the resistivity.

[0064] The CNT fiber preferably has a specific conductivity higher than $0.6\cdot 10^4 \text{ S}/(\text{g}\cdot\text{cm})$, preferably higher than $2\cdot 10^4 \text{ S}/(\text{g}\cdot\text{cm})$, more preferably higher than $1.3\cdot 10^4 \text{ S}/(\text{g}\cdot\text{cm})$. The specific conductivity is calculated as the conductivity divided by the density of the CNT fiber. Conductivity is the reciprocal value of resistivity.

[0065] The density of the CNT fiber is determined by dividing the weight of a piece of filament by its volume.

[0066] In a preferred embodiment, the diameter of the CNT fiber preferably is less than 50 μm . Preferably, the

CNT fiber has a diameter in the range of 1 to 50 μm , more preferably in the range of 2 to 40 μm , most preferably in the range of 3 to 30 μm .

[0067] In an embodiment, the CNT fiber comprises up to 25 wt.% of a charge carrier donating material(s). It is believed that the charge carrier donating material(s) in the CNT fiber may further reduce the resistivity of the CNT fiber.

[0068] The charge carrier donating material may be comprised within the individual carbon nanotubes, in particular when the CNT fiber comprises open ended carbon nanotubes, and/or the a charge carrier donating material may be comprised in between the individual carbon nanotubes, in particular when the CNT fiber comprises closed carbon nanotubes.

[0069] The charge carrier donating material may comprise an acid, preferably a super acid, salts, such as for example CaCl_2 , or bromide containing substances, or iodine.

[0070] In another embodiment, the CNT fiber has a modulus of at least 120 GPa, more preferably at least 150 GPa, most preferably at least 200 GPa.

[0071] In a preferred embodiment, the CNT fiber has a tensile strength of at least 0.3 GPa, preferably at least 0.8 GPa, more preferably at least 1.0 GPa, most preferably at least 1.5 GPa.

[0072] Tensile strength has been determined on samples of 20mm length by measuring breaking force at 3mm/s extension rate and dividing the force by the average surface area of the filament. Modulus has been determined by taking the highest slope in the force vs. elongation curve, and divide the value by average surface area.

[0073] Fiber surface area is determined from the average diameter. The average fiber diameter is determined by averaging fiber thickness measured from SEM images at at least 5 positions.

[0074] Reported values in the examples are averages over at least 3 pieces of filaments. Also highest values are reported.

Examples

Example 1

[0075] A CNT fiber was prepared by thoroughly mixing 1 g of predominantly double wall carbon nanotubes having an average length of 3 μm and a G/D ratio of 17 with 10 ml chlorosulfonic acid to obtain a spin-dope comprising 6 wt.% carbon nanotubes. The spin-dope was extruded through a spinneret comprising a single spinning hole having a diameter of 65 μm . The extruded CNT fiber entered into a coagulation bath comprising water. The CNT fiber was collected on a winder at a winding speed of 13 m/min and an extrusion speed of 10 m/min, giving an effective draw ratio of 1.3. In a subsequent processing step the fiber was washed with water and dried in an oven at 110°C for 120 minutes.

[0076] The resistivity of the CNT fiber was 43 +/- 4 $\mu\Omega\cdot\text{cm}$, the diameter of the fiber was 16 +/- 0.2 μm , the tensile strength was 0.58 +/- 0.07 GPa (highest 0.62 GPa) and the modulus was 146 +/- 27 GPa (highest 169 GPa).

Example 2

[0077] A CNT fiber was prepared as in example 1, but the extrusion rate was 11 m/min, giving an effective draw ratio of 1.1.

[0078] The resistivity of the CNT fiber was 44 +/- 2 $\mu\Omega\cdot\text{cm}$, the diameter of the fiber was 19.6 +/- 2.7 μm , the tensile strength was 0.38 +/- 0.08 GPa (highest 0.47 GPa) and the modulus was 80 +/- 26 GPa (highest 130 GPa).

Example 3

[0079] A CNT fiber was prepared by thoroughly mixing 0.5 g of predominantly double wall carbon nanotubes having an average length of 3 μm and a G/D ratio of 17 with 10 ml chlorosulfonic acid to obtain a spin-dope comprising 3 wt.% carbon nanotubes. The spin-dope was extruded through a spinneret comprising a single spinning hole having a diameter of 65 μm . The extruded CNT fiber entered into a coagulation bath comprising DM-SO/PVA. The CNT fiber was collected on a winder at a winding speed of 8.8 m/min and an extrusion speed of 1.8 m/min, giving an effective draw ratio of 4.9. In a subsequent processing step the fiber was washed with water and dried in an oven at 110°C for 120 minutes.

[0080] The resistivity of the CNT fiber was 46 $\Omega\mu\cdot\text{cm}$, the tensile strength was 0.25 GPa and the modulus was 47 GPa.

Comparative example 1

[0081] A CNT fiber was prepared as in example 1, but the extrusion rate was 9 m/min, giving an effective draw ratio of 0.9.

[0082] The resistivity of the CNT fiber was 460 +/- 31 $\mu\Omega\cdot\text{cm}$, the diameter of the fiber was 25 +/- 2 μm , the tensile strength was 0.05 +/- 0.01 GPa and the modulus was 12.5 +/- 5 GPa.

Comparative example 2

[0083] A CNT fiber was manufactured by thoroughly mixing 0.6 g of single wall carbon nanotubes having an average length of 0.5 μm and a G/D ratio of 25 (HiPCO) with 10 ml chlorosulfonic acid to obtain a spin-dope comprising 4 wt.% carbon nanotubes. The spin-dope was extruded through a spinneret comprising a single spinning hole having a diameter of 65 μm . The extruded CNT fiber entered into a coagulation bath comprising DM-SO/PVA. The CNT fiber was collected on a winder at a winding speed of 9 m/min and an extrusion speed of 1.8

m/min, giving an effective draw ratio of 4.6. In a subsequent processing step the fiber was washed with water and dried in an oven at 100°C for 120 minutes.

[0084] The resistivity of the CNT fiber was 310 $\mu\Omega\cdot\text{cm}$, the diameter of the CNT fiber was 9 μm , the tensile strength was 0.22 +/- 0.05 GPa and the modulus was 73 +/- 25 GPa.

Claims

1. A carbon nanotubes (CNT) fiber **characterized in that** the CNT fiber has a resistivity less than 120 $\mu\Omega\cdot\text{cm}$.
2. The CNT fiber according to claim 1 **characterized in that** the CNT fiber has a resistivity less than 100 $\mu\Omega\cdot\text{cm}$, preferably less than 50 $\mu\Omega\cdot\text{cm}$, even more preferably less than 20 $\mu\Omega\cdot\text{cm}$, most preferably less than 10 $\mu\Omega\cdot\text{cm}$.
3. A carbon nanotubes (CNT) fiber **characterized in that** the CNT fiber has a modulus of at least 120 GPa.
4. The CNT fiber according to claim 3 **characterized in that** the CNT fiber has a modulus of at least 150 GPa, preferably at least 200 GPa.
5. The CNT fiber according to any of claims 1 to 4 **characterized in that** the CNT fiber comprises ropes having a length of 1 μm to 5 mm.
6. The CNT fiber according to any of claims 1 to 5 **characterized in that** the CNT fiber is manufactured in a wet spinning process.
7. The CNT fiber according to any of claims 1 to 6 **characterized in that** the CNT fiber comprises up to 25 wt.% of a charge carrier donating material.
8. The CNT fiber according to any of claims 1 to 7 **characterized in that** the diameter of the CNT fiber is in the range of 1 to 50 μm .
9. The CNT fiber according to any of claims 1 to 8 **characterized in that** the CNT fiber has a tensile strength of at least 0.3 GPa, preferably at least 0.8 GPa, more preferably at least 1.0 GPa, most preferably at least 1.5 GPa.
10. A composite article comprising carbon nanotubes fibers according to any of the preceding claims.
11. A process for manufacturing carbon nanotubes (CNT) fibers comprising the steps of supplying a spin-dope comprising carbon nanotubes to a spinneret, extruding the spin-dope through at least one spinning hole in the spinneret to form spun CNT fiber

(s), coagulating the spun CNT fiber(s) in a coagulation medium to form coagulated CNT fibers **characterized in that** the CNT fiber(s) is/are drawn at a draw ratio of at least 0.8 and wherein the carbon nanotubes have a length of at least 0.5 μm .

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12. The process for manufacturing carbon nanotubes fiber according to claim 11 **characterized in that** the carbon nanotubes have a length of at least 1 μm , preferably at least 2 μm , more preferably at least 5 μm , even more preferably at least 15 μm , most preferably at least 20 μm . 10
13. The process for manufacturing carbon nanotubes fiber according to any of claims 11 to 12 **characterized in that** the CNT fiber(s) is/are drawn at a draw ratio of at least 1.0, preferably at least 1.1, more preferably at least 1.2, even more preferably at least 5, most preferably at least 10. 15
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14. The process for manufacturing carbon nanotubes fiber according to any of claims 11 to 13 **characterized in that** the carbon nanotubes have a G/D ratio of at least 4, preferably at least 10. 25
15. The process for manufacturing carbon nanotubes fiber according to any of claims 11 to 14 **characterized in that** the winding speed of the CNT fiber is at least 0.1 m/min, preferably at least 1 m/min, more preferably at least 5 m/min, even more preferably at least 50 m/min, most preferably at least 100 m/min. 30
16. The process for manufacturing carbon nanotubes fiber according to any of claims 11 to 15 **characterized in that** the spinning hole(s) in the spinneret has/ have a diameter or a minor dimension in the range of 10 to 1000 μm , preferably in the range of 25 to 500 μm , most preferably in the range of 40 to 250 μm . 35
17. The process for manufacturing carbon nanotubes fiber according to any of claims 11 to 16 **characterized in that** the CNT fiber(s) is/are drawn in a separate drawing process. 40

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EUROPEAN SEARCH REPORT

Application Number
EP 11 18 0343

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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