

Electrical Properties of Carbon Nanotube Based Fibers and Their Future Use in Electrical Wiring

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The production of continuous fibers made purely of carbon nanotubes has paved the way for new macro-scale applications which utilize the superior properties of individual carbon nanotubes. These wire-like macroscopic assemblies of carbon nanotubes were recognized to have a potential to be used in electrical wiring. Carbon nanotube wiring may be extremely light and mechanically stronger and more efficient in transferring high frequency signals than any conventional conducting material, being cost-effective simultaneously. However, transfer of the unique properties of individual CNTs to the macro-scale proves to be quite challenging. This Feature Article gives an overview of the potential of using carbon nanotube fibers as next generation wiring, state of the art developments in this field, and goals to be achieved before carbon nanotubes may be transformed into competitive products.

1. Introduction

The ever increasing use of technology in all areas of our daily life has had an immense effect on our demand for electrical energy, and this has resulted in the urgent need to find more efficient methods for its generation and distribution. This need has stimulated the quest for new materials and highly efficient devices, which have significantly better performance than those currently in use, as well being cost-effective, safe, and environmentally friendly. In this perspective, carbon is a very promising material.

The recent synthesis of fullerenes, carbon nanotubes and separation of graphene has generated enormous interest in these carbon materials.^[1] Carbon allotropes of this type offer not only a highly exciting and vast area for scientific exploration but also the potential for a wide spectrum of novel engineering applications due to their properties.

Carbon nanotubes are particularly attractive, due to their tubular shape, low density, tuneable electrical properties, ballistic

electron transport, lack of skin effect, current carrying capacity exceeding superconductors, mechanical strength/stiffness better than any metal, thermal conductivity exceeding diamond and many other properties. This amazing list can be extended by advantages such as the wide availability of carbon sources, the potential low-cost of large-scale production and their zero net carbon footprint, together these attributes make carbon nanotubes an obvious candidate for “the material of the future”.

One very interesting potential application of carbon nanotubes is in electrical wiring. Conventional electrical wires made of copper and aluminium suffer from several problems including: weight (an issue

in aerospace applications), skin effect (hindering their use in modern telecommunications), mechanical performance (critical in overhead power lines), and electromigration (severely damaging microscopic wires in electronics applications). Moreover, the growing demand for these conventional metal conductors and their continually increasing prices suggests that a low-cost material that can outperform conventional conductors would be highly desirable. Hence, carbon nanotubes are the material of great interest.

However, there are several challenges in the production of carbon nanotube electrical wires and their application, which include; preparation of macroscopic structures that retain the properties of individual nanotubes, control over the morphology and dimensions of these structures, development of large-scale cost-effective manufacturing processes and providing the wires with suitable electrical insulation and connections for integration into electrical systems. Not less important, is the in-depth understanding of the physics behind the transport properties of these new carbon structures and possible preparation of new standards for the use of the CNT wires. Some of the solutions to these issues have been already suggested.

Several research groups have already succeeded in the production of macroscopic CNT fibers (also referred to as yarns or threads) which are long assemblies of axially aligned nanotubes, of diameters in the micrometer range.^[2–4]

The theoretical and experimental research on CNT fibers predict that proper control of the morphology of these macroscopic assemblies of CNTs should produce the material of excellent electrical conductivity comparable to the conductivity of individual nanotubes.^[5]

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Moreover, the fibers should considerably exceed the performance of any metals used currently in electrical engineering in terms of mechanical and thermal properties, while keeping the density very low.

The best as-made CNT fibers have indeed excellent mechanical performance, which is superior to any conventional conductive metals and they have very low density.^[2,3,6] However, the electrical conductivity is still below aluminium and copper.^[3,7,8] This lower electrical conductivity, which stems from a limited control over the morphology of the CNTs and CNT fibers is the major obstacle currently impeding the extensive application of nanotubes for electrical wiring.

Recently, our group succeeded in producing CNT fiber comprising only two types of armchair SWNTs using the floating catalyst chemical vapor deposition (CVD) method, which allowed the production of fibers with a very high specific electrical conductivity (conductivity divided by density).^[9] However, further research is still needed for this to outperform traditional conductors.

Some groups temporarily overcame the problem of low conductivity via doping of the fibers and even showed that CNT fibers can exceed specific conductivities of copper and aluminium.^[3,7] However, the ideal solution would be to obtain the full control over the morphology of the fibers, then there would be no need for additional doping steps in production process which make the manufacture of carbon nanotube wires complicated and unnecessarily increase the cost of the final product, which otherwise can be very low.

As an example, the one-step dry spinning of CNT fibers out of a CVD furnace, which is probably the most easy to scale up and definitely the fastest CNT fiber production method as the synthesis takes place within seconds and the fibers may be spun with the speed up to 100 m min^{-1} , may be compared to the production of synthetic amorphous carbon. The price of a kilogram of such carbon is approximately 1 USD. Taking into account that carbon nanotubes are at least twice and six times less heavy than aluminium and copper respectively, the production costs of CNT fibers may soon become competitive with regard to metal wires.

The most recent results of our research on the development of CNT wires also show that the further steps necessary to use CNT fibers as electrical wires, which involves the insulation of the fibers and providing them with electrical contacts, can be as simple and inexpensive as in case of standard metal wires.^[8,10] (We will refer, from this point forward, to the insulated CNT fiber or CNT cord, that is, many CNT fibers joined in parallel, as "CNT wire".)

The above mentioned developments of CNT wires has already led to a pilot application of these wires in a macroscopic electrical machine—a high frequency electrical transformer in which all the copper windings were replaced with CNT wires.^[11] Potentially, the use of CNT wires in such transformers would be of great importance for aviation industry as the use of CNT wires may substantially decrease the weight of these omnipresent devices, and thus the overall weight of large aircraft.

All the above described research results, inventions and pilot application show that carbon nanotube fibers are highly likely to be the material for the next generation of electrical conductors. This feature article focuses mainly on an in-depth analysis of the electrical properties of currently produced CNT fibers and the potential of CNT fibers with respect to electrical wiring



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applications. The paper examines also the challenges in the area of CNT wire research and suggests some possible solutions to the issues arising. The paper is divided into eight sections represented schematically in **Figure 1**.

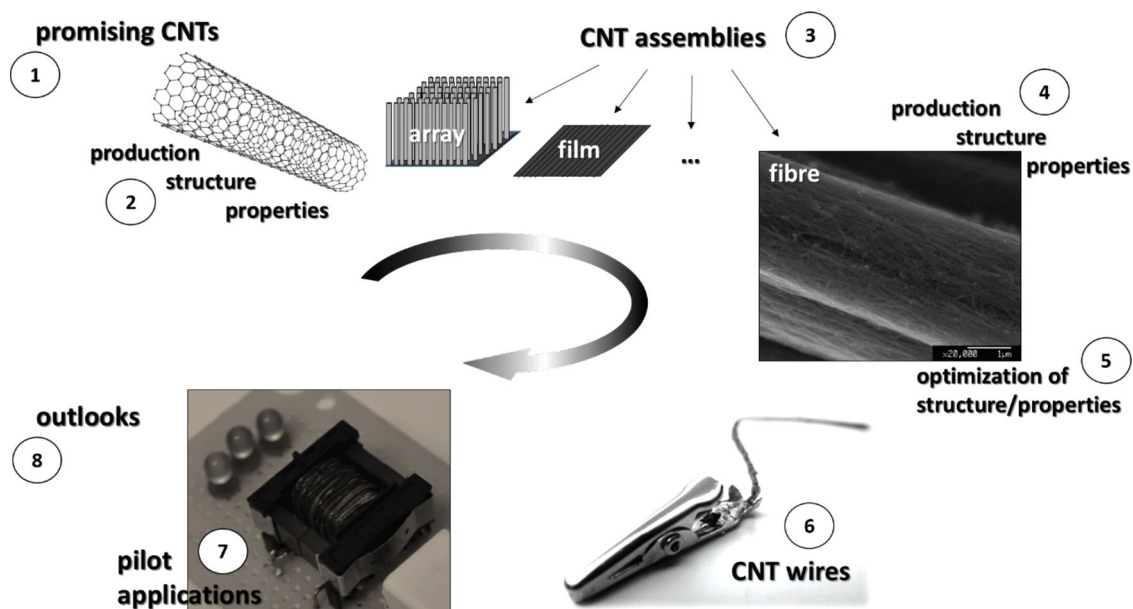


Figure 1. Schematic diagram representing the table of contents of this feature paper. The numbers in black circles correspond to the section numbers in the paper. (1) The paper starts from the introduction describing the reasons for undertaking this work. Section (2) describes the structure, properties and production methods of individual carbon nanotubes. Section (3) focuses on CNT assemblies one of which are CNT fibers described in Sections (4) and (5). Section (4) deals with current CNT fibers' production methods as well as structure and properties of the state-of-the-art fibers. Section (5) recognizes the needs for further research in the area of CNT fibers structure and properties. Sections (6) and (7) describe the recent developments in which led to the production of the first macroscopic CNT wires and devices. Finally, some outlooks are presented in the concluding Section (8).

2. Individual Carbon Nanotubes

2.1. Structure and Classification

The structure of carbon nanotubes (CNTs) is based on a planar hexagonal lattice of carbon atoms, called graphene, rolled to form seamless tubes (Figure 2a).^[12] Depending on how the graphene sheets are rolled into nanotubes, which is referred to as CNT chirality, the following three basic types of CNT structures are distinguished. These are: zig-zag, if the hexagonal lattice forms a zig-zag pattern along the circumference of the nanotubes, armchair in which the lattice is turned round by

90° with regard to zig-zag pattern, and chiral when any other pattern appears along the circumference (Figure 2a). The exact intrinsic geometry of CNTs greatly influences their properties, particularly the nature of electrical conductivity.^[14,15] Armchair nanotubes are always semi-metallic (for simplicity often called metallic), that is, their conduction and valence bands slightly overlap resulting in a continuous density of states at the Fermi level. Zig-zag and chiral nanotubes, depending on their diameter and in case of chiral nanotubes their exact chirality, may have different widths of bandgaps and their properties may range from practically semi-metals up to wide bandgap semiconductors.

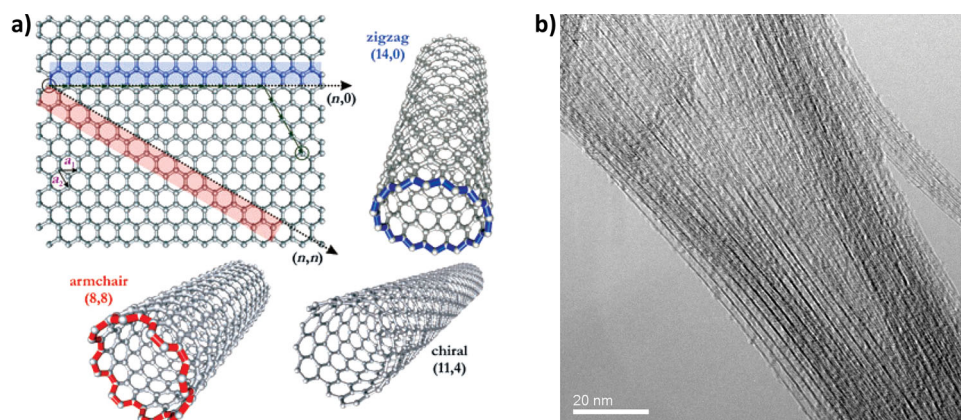


Figure 2. a) Formation of three main types of carbon nanotube structures, from a graphene layer. \mathbf{a}_1 and \mathbf{a}_2 denote unit vectors, while (n,n) denote chiral indices used to describe the exact chiralities of every nanotube. Reproduced with permission.^[13] Copyright 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) Transmission electron microscope image of a bundle of armchair SWNTs.

The carbon nanotubes may be found as single-wall (SWNT), that is, made of one graphene sheet or double-wall (DWNT) and multi-wall (MWNT) consisting, respectively, of two or more concentric SWNTs of different diameters and chiralities. Diameters of SWNTs typically range from 0.7 to 3 nm and of MWNTs, from 4 nm to tens of nanometers.^[16] The typical lengths are in the order of hundreds of micrometers and up to a few millimetres, for SWNT and MWNTs respectively. However, a synthesis of individual SWNTs as long as 55 cm has been also reported recently.^[17]

2.2. Methods of Synthesis

The basic methods of synthesis of carbon nanotubes include laser ablation, arc discharge and chemical vapor deposition (CVD).^[12] The first two involve the evaporation of carbon molecules from the solid, whereas CVD method, cracking the hydrocarbon precursors. The carbon atoms get then rearranged into a desired nanotube structure. All the methods require high temperatures to initiate the process and maintain the CNT growth. Most CNT fibers are produced out of the nanotubes obtained via CVD route.

2.3. Properties of Individual Nanotubes

Individual carbon nanotubes are a type of quantum wires.^[12] They are long but extremely narrow conductors with diameters in the range of several atomic distances, and additionally are hollow. The electron wavevectors are quantized along the circumferences of the nanotubes and the charge carriers are free to travel only along the axial directions. Similarly to other quantum wires, the CNTs may show ballistic electron transport i.e. without scattering, which has been confirmed experimentally.^[12,18] According to theoretical calculations, electrons in CNTs should travel over micrometre range distances without experiencing scattering at room temperature.^[19] The maximum mean free path measured experimentally at room temperature amounted to 1 μm .^[18] For comparison, electrons in copper at room temperature have mean free paths of only 40 nm.^[20]

Quantum confinement always results in a finite conductance which is a multiple of the conductance quantum $G_0 = 2e^2/h$ (e stands for electron charge, h is the Planck constant), increasing with the number of quantum channels.^[12] This applies even for fully ballistic transport, which means that the non-zero resistance is associated with the connections and not the scattering within the quantum wire. An individual SWNT can have a maximum conductance of $G = 4e^2/h \approx 0.15 \text{ mS}$.^[12,19] Based on this value and experimentally measured ballistic transport length-scales, it can be calculated that the resistivity in the individual SWNT, at room temperature, can be as low as $10^{-6} \Omega \text{ cm}^{-1}$, which exceeds conventional conductive metals.^[18] The lowest resistivity reported for MWNT amounted to $5 \times 10^{-6} \Omega \text{ cm}^{-1}$ ^[21] which was lower than SWNT probably due to the fact that MWNTs have higher diameters than typical SWNTs.

The above mentioned values of conductivity are obtained in the material of much lower density (particularly in case of SWNTs) than metals used as electrical conductors, which may

be highly important for many applications. The density of carbon nanotubes amounts to about 1.3 g cm^{-3} for SWNT^[22] and 2.1 g cm^{-3} for MWNT,^[23] whereas for copper and aluminium about 8.96 g cm^{-3} and 2.7 g cm^{-3} respectively.

If the length of CNT is larger than the ballistic regime then diffusive transport will be observed.^[24] Ballistic transport may also be suppressed owing to increased temperature^[25] or high electric fields.^[26] Nonetheless, the maximum current density measured experimentally in individual SWNT at room temperature amounted to $10^9\text{--}10^{10} \text{ A cm}^{-2}$, which is higher than even the critical current density of superconductors.^[26–28]

Regarding the factors which may impede the electrical performance of CNTs, it was found that electron transport in CNTs may be changed by disorders such as structural defects formed during synthesis processes^[29] or physical distortions, for example, evoked by strong mechanical forces.^[30] However, it was found that semiconducting nanotubes are the most sensitive to disorder.^[31] For armchair nanotubes, only defects with a potential shorter than the distance between carbon atoms, such as vacancy, considerably decrease the conductance at the Fermi level.^[32,33] The weak vulnerability to electron scattering in armchair nanotubes is related to their high symmetry and a decrease of the defect potential averaged over the circumference of the nanotube.^[19,34]

Apart from the unique electrical properties, the CNTs, are characterized by excellent mechanical performance. The experimentally measured values of tensile moduli amounted to approximately 0.3–0.95 TPa, tensile strengths approximately 10–100 GPa and tensile strains approximately 6–12%.^[35–37] The values of modulus and strength under uniform compression, measured by embedding the nanotubes in polymer or epoxy matrix, were even higher.^[38] Due to low density, nanotubes have very high specific mechanical properties (strength or stiffness divided by density), far exceeding steel or other high performance materials.

Moreover, the thermal conductivity of CNTs in the axial direction exceeds the best known bulk heat conductors including diamond. Experimentally measured thermal conductivities of isolated SWNT and MWNT, in the axial direction, were 3500 and 3000 $\text{W m}^{-1} \text{ K}^{-1}$ respectively,^[39,40] Such extremely high thermal conductivity contributes to the effective heat removal, which is also facilitated by the extremely high surface area of CNTs.

All the above presented data show that carbon nanotubes are very interesting materials for electrical engineering applications as they have all the characteristics of a perfect electrical conductor, very high conductivity, current carrying capacity, strength, and thermal conductivity, all combined with very low weight.

3. Assemblies of Carbon Nanotubes

During the synthesis process, SWNTs often spontaneously assemble into bundles (also referred to as ropes) due to Van der Waals interactions.^[41] The phenomenon was also observed for DWNTs, MWNTs and for mixed types of CNTs.^[42,43] In severe synthesis conditions, bundling provides energetic stability for individual nanotubes. Transmission electron microscope image of a bundle of SWNTs is presented in Figure 2b).

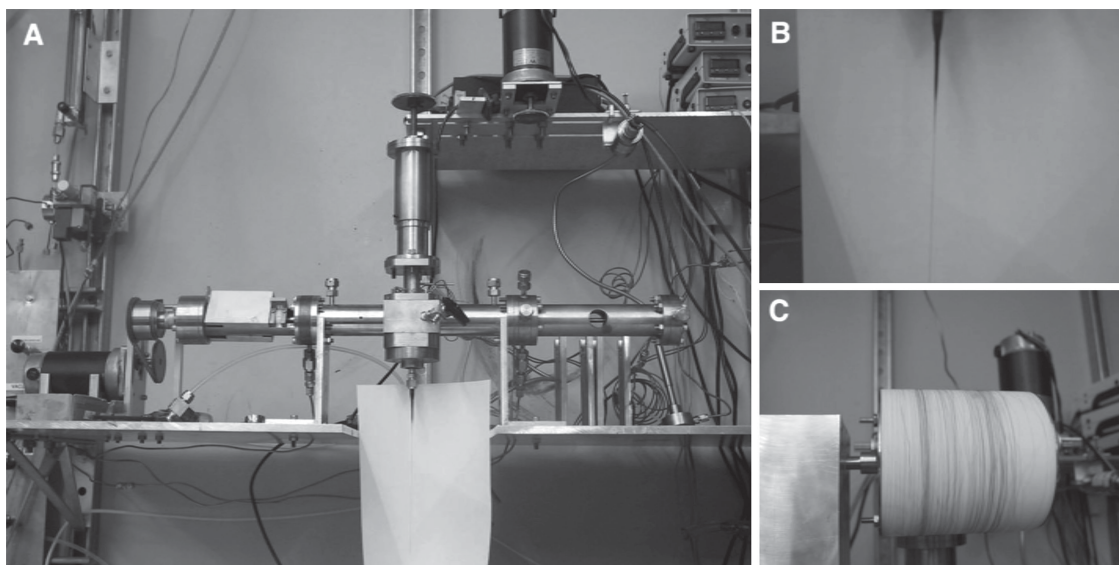


Figure 3. A) The system used by Ericson et al.^[50] to spin CNT fibers from liquid crystalline phase. B) Fiber extruded from capillary tube. C) CNT fiber wound on a rotating spool. Reproduced with permission.^[50] Copyright 2012, American Association for the Advancement of Science.

Depending on the synthesis process, nanotubes may also be grown as macroscopic assemblies of CNTs such as films,^[44] arrays,^[4] cottons,^[45] or fibers.^[46] In these assemblies the individual CNTs and CNT bundles agglomerate due to Van der Waals interaction, friction forces and local entanglements. Films, also referred to as sheets,^[44] are flat “papers” made of CNTs with their axial dimensions arranged in the plane of the “paper” and along either the length or width of the sheet. CNT arrays,^[4] also called forests or carpets, are assemblies of vertically arranged nanotubes. CNT cottons^[45] are very sparse assemblies of CNTs characterized by a random distribution of CNTs/CNT bundles in all three dimensions. The CNT fibers, also referred to as yarns or threads, described in this thesis^[46] are long and thin assemblies of axially aligned CNTs and CNT bundles.

CNT fibers can be obtained from direct synthesis methods, but can also be spun, in two-step processes, out of other types of as-synthesized assemblies or via wet and electrical techniques out of dispersed individual CNTs. The spinning techniques proposed so far are described in the following section.

4. Carbon Nanotube Fibers

4.1. Methods of CNT Fibers Production

Commonly, the production processes of CNT fibers are divided into two basic categories, that is, wet and dry spinning.^[31] There are also a few reports of spinning of the fibers using electrical methods, which probably should be treated as a separate category.^[47–49]

The wet methods rely on extrusion of a liquid solution of nanotubes into a bath with a coagulant, which is a liquid that can mix with the solvent but cannot disperse nanotubes.^[31] The CNTs therefore get precipitated in the form of long fibers. There are three basic spinning approaches reported, that is,

spinning: i) out of liquid crystalline suspensions of SWNTs in superacids^[3,50–52] or MWNTs in ethylene glycol;^[53] ii) out of surfactant-stabilized suspensions,^[54,55] which normally use sodium or lithium dodecyl sulphates as surfactants; and iii) out of dispersions prepared with the aid of biomolecules,^[56,57] for example, DNA or hyaluronic acid. Quite a wide range of substances may be used as coagulants, including water,^[50,51] alcohols,^[57] polymeric compounds,^[54,56,58] acids,^[55,57] and so forth. So as to obtain fibers made purely of CNTs, the post process annealing has to be applied to remove residual chemicals from the as-made fibers.

The most popular wet spinning process is the method proposed first by Ericson et al. which is the spinning from superacid LC phase.^[50] The LC phase is prepared from SWNTs produced via high-pressure decomposition of CO and superacid which protonates the nanotubes and causes their electrostatic repulsion thus causing the formation of homogenous SWNTs solutions.^[50,59] Next, the LC is continuously extruded through a capillary into the coagulation bath and then, depending on the coagulant used, either directly wound on a rotating spindle or washed prior to the collection. **Figure 3** presents an example of a setup used by Ericson et al. for spinning of the fibers.^[50] Similarly to other wet spun fibers, to obtain pure material, the fibers need to be annealed at very high temperatures, otherwise, they stay severely doped with the superacids used for dispersion.

Dry methods include a one-step process in which the fibers are directly drawn from CVD reactor,^[9,46,60,61] and two-step techniques which rely on spinning out of other CNT assemblies: CNTs arrays,^[4,62–64] CNT cotton,^[45,65] and CNT films.^[66,67]

The direct spinning of CNT fibers from a CVD reactor is shown schematically in **Figure 4**. The vertical arrangement of the reactor is shown as an example; however, it may as well be orientated horizontally. In the direct spinning process the feedstock comprising hydrocarbons, ferrocene, a sulphur compound and hydrogen is introduced into the hot zone of a CVD furnace (temperatures above 1000 °C).^[2,9,46] The ferrocene becomes a source

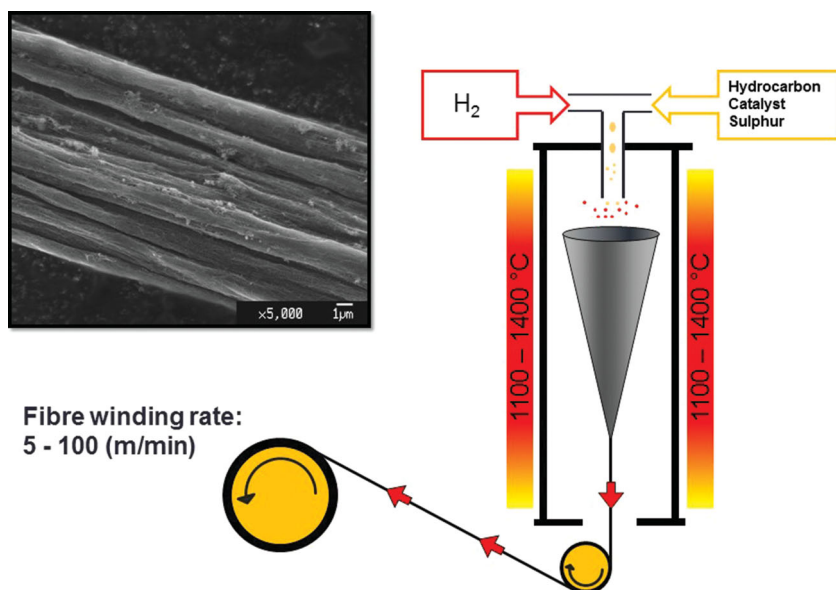


Figure 4. Top-left: scanning electron microscope image of CNT fiber produced directly from CVD reactor presented on the right. Feedstock is introduced at the top of vertical furnace. CNTs are synthesized in the hot zone of the reactor and extracted at the bottom in the form of fiber. The fibers are condensed and wound on rotating collector.

of iron catalyst clusters whose size is controlled with the aid of sulphur and hydrogen. The decomposition of hydrocarbons provides carbon, which in the reducing hydrogen atmosphere allows the growth of nanotubes on the catalyst clusters. The grown CNTs form an aerogel, which is then drawn out of the furnace using a metal rod inserted from the bottom of the furnace. The nanotubes which stick to the rod drag other nanotubes along, due to van der Waals interactions, thus introducing the first alignment to the material. To increase the proximity of the nanotubes to each other the CNT material is then condensed and spun on rotating spindles. The most frequently applied condensation techniques include densification with the use of liquids by the spraying of acetone, which wets the nanotubes and pulls together the individual CNTs and CNT bundles when evaporating or alternatively by inserting it into a bath with water which pulls the nanotubes together due to hydrophobicity effect.^[2,61]

Among the two-step dry methods of CNT fiber production, the most widely applied is that of drawing of the fibers from CNT vertical arrays (forests).^[4,62–64,68] In the first step, the forests are prepared using CVD techniques. In order to obtain CNT forests, the catalyst particles are placed on a substrate which is inserted into a furnace. The hydrocarbons are introduced into the furnace with the flow of carrier gases such as a mixture of 5 mol% acetylene in helium. The synthesis takes place in the hot zone of the reactor, normally at temperatures above 600 °C.^[4]

In the second step of fiber spinning, depicted in **Figure 5**, a chosen cluster of CNT is pulled out of the assembly.^[68] The following nanotubes get attached at the ends of the previous ones, thus forming a sparse wire-like network of axially aligned CNTs. Most often, the networks are condensed via twisting.^[45,62,64,68–73]

The process taking place during the drawing of the fibers from the arrays is not yet fully understood. However it is

known that not all the arrays are spinnable. Such factors as over-waviness of CNTs, improper length or presence of impurities were suggested as factors, which prevent the formation of continuous fibers.^[68,74,75] The existing theories indicate two potential explanations of the mechanisms of spinning of CNT fibers from CNT arrays. The first one suggests that during drawing the bigger CNT bundles get joined at the ends by smaller bundles. The small bundles slide along the big bundles during separation. They accumulate at the tips of the big bundles knotting them together and thus a continuous chain of nanotubes is formed.^[75] The second theory, based on SEM observations of the spinning process, suggests that natural slight entanglement of nanotubes results in the formation of connections between the ends of drawn CNT bundles due to the compression of the entanglements.^[76]

In a similar fashion to the spinning from a vertical array of CNTs the fibers may be spun from the CNT cotton or films.^[45,65–67] The cotton is prepared via the CVD method.^[45] In

this process catalyst particles are mixed with hydrocarbon and their solution is introduced into the hot zone of the reactor by a carrier gas. The cotton is grown on substrates analogously to CNT arrays or on the walls of the CVD furnace. Then a cluster of nanotubes is pulled out of the assembly which drags along further nanotubes.

CNT films for fiber spinning were prepared in a process analogous to the one used for one-step direct spinning of CNT fibers from CVD reactor described above.^[46,67] To obtain the CNT films the partly aligned sparse material extracted directly from the furnace is not condensed but directly wound on a rotating collector. Many layers of material form thick free-standing films of CNTs, which then may be spun like CNT arrays and cottons.

Finally, it was shown that CNT fibers may be spun using electrical methods. Ma et al. demonstrated the spinning out of aqueous solutions of SWNTs.^[47,48] The CNT solution was placed in a vessel which constituted the first electrode. A second electrode was made of a wire attached to a movable stage which allowed the withdrawal of the fiber out of the solution. A low voltage (10 V) at high frequency (2 MHz) was applied between the electrodes. To obtain longer fibers, the wire used as the second electrode was replaced by a metal ring with saline solution suspended in it. The fiber was withdrawn through the ring and collected on a rotating rod.

In the process suggested by Imaizumi et al., the MWCNTs were dispersed in polyvinyl butyral.^[49] A high voltage of 15 kV was applied between the metal nozzle (first electrode) of an infusion pump containing the MWNT/polymer solution and the rotating collector (second electrode). Thus composite CNT/polymer fibers were spun. Further, the output material was annealed to obtain pure CNT fibers. **Figure 6** shows the setup used by Imaizumi et al.^[49]

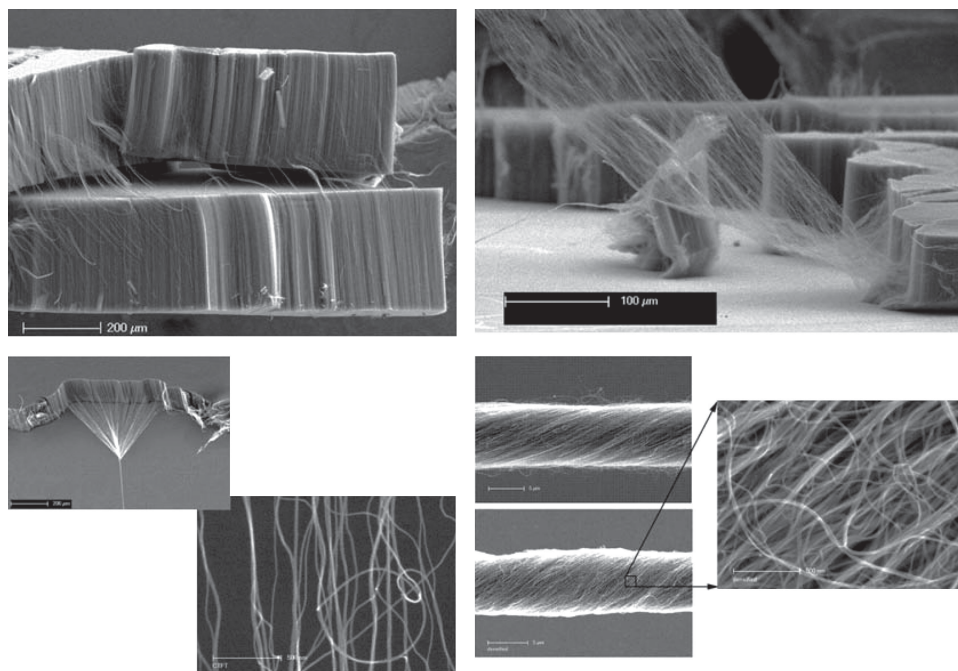


Figure 5. Top left: an image of spinnable CNT array used by Huynh et al.^[68] Top-right: initial part of a spun CNT fiber. Bottom left: twisting of the fiber. Bottom right: images of CNT fibers before and after densification with acetone with an insight into the internal structure of the spun fibers. Reproduced with permission.^[68] Copyright 2012, Elsevier.

4.2. Properties of CNT Fibers

4.2.1. Density

The hollow structure of individual carbon nanotubes provides CNT fibers which exhibit low weight. The theoretical density of an assembly of SWNTs amounts to 1.5 g cm^{-3} .^[3] This value may be decreased when the CNT assembly is less densely packed and increased due to the presence of MWNTs, collapsed structures and impurities. However, as shown in **Table 1**, the approximate value of volumetric density of condensed as-made CNT fiber amounts to 1 g cm^{-3} which is up to 9, 7, and 3 times

less than the density of copper, iron and aluminium respectively. Low weight is a critical property for many areas of technology including design of devices for aviation, shipping and overhead power lines.

Weight is also a useful parameter in allowing the reliable comparison of properties of CNT fibers with bulk conventional conductors. Due to the yarn-like structure of CNT fibers the exact determination of the cross-sectional area used in the fiber for electron transport or load bearing is quite challenging. Following the experience of textile industry many authors have used linear density measured in the unit of tex ($1 \text{ tex} = 1 \text{ g km}^{-1}$) which is the mass of the unit of length of a given fiber as a normalizing factor for physical properties which conventionally were calculated over cross-sectional area.^[2,3,7,62] The linear density may be accurately measured experimentally using a simple method such as a balance and ruler or the well-established textile industry vibration method.^[77]

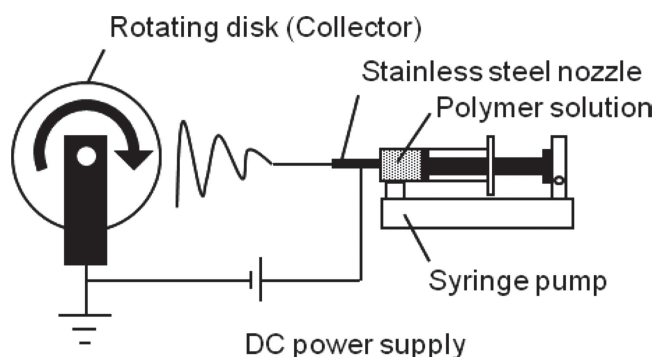


Figure 6. Schematic drawing of a system used for spinning CNT fiber via electrical method used by Imaizumi et al.^[49] The fibers dispersed in polymer are extruded from a nozzle with the aid of DC voltage applied between the nozzle and a rotating winder on which the fibers are collected. Reproduced with permission.^[49] Copyright 2012, American Chemical Society.

4.2.2. Mechanical Properties of CNT Fibers

The superior mechanical properties of individual nanotubes are easier to transfer to macro-scale than electrical or thermal properties. Several of the fibers have already exceeded 200 GPa of stiffness and 1.5 GPa of strength, which exceeds any conventional metals used in electrical engineering.^[2,64,78] Taking into account the difficulty in estimating the real cross-sectional area (see also second subsection of Section 4.2.4. where the same problem is encountered in relation to calculation of electrical conductivity) of the fibers and using specific gravity (where specific gravity (SG) is a dimensionless parameter standing

Table 1. Mechanical properties of CNT fibers characterized electrically in Table 2.

| Fiber treatment | Linear density [tex] | Volumetric density [g cm ⁻³] | Mechanical properties | | | | Refs. |
|--|-------------------------|--|---------------------------|---|-----------------------|---|---------|
| | | | Tensile strength [GPa] | Specific tensile strength [GPa SG ⁻¹] | Stiffness [GPa] | Specific stiffness [GPa SG ⁻¹] | |
| electrospinning | | | | | | | |
| spun with PVB, annealed (400 °C) | 5.01 | 0.47 | 0.0127 ± 0.0014 | 0.027 ± 0.003 | 3.48 ± 0.28 | 7.40 ± 0.59 | [49] |
| CNTs refluxed in 6 N HNO ₃ for 24 h before spinning | – | – | >0.4 | – | – | – | [48] |
| wet-spun fibers from liquid crystalline phase | | | | | | | |
| annealed (280 °C 2 h) | – | – | 0.15 ± 0.06 | – | 69 ± 41 | – | [53] |
| nitrogen doped CNTs | – | – | 0.17 ± 0.07 | – | 142 ± 70 | – | [53] |
| 102% H ₂ SO ₄ doped | – | 0.87–1.1 | 0.116 ± 0.01 | 0.1–1.16 | 120 ± 10 | 109–138 | [50] |
| vacuum annealed at 1100 °C 1 h | – | – | – | – | – | – | [50] |
| spinning with the use of HSO ₃ Cl, H ₂ SO ₄ | – | – | 0.05–0.32 | – | 120 | – | [51] |
| doped with HSO ₃ Cl, | – | 1.3 ± 0.1 | 1 ± 0.2 (max 1.3) | 0.77 ^{a)} | 120 ± 50 (max 200) | 92.3 ^{a)} | [3] |
| doped with HSO ₃ Cl and I ₂ | – | 1.4 | | | | | [3] |
| other wet spun fibers | | | | | | | |
| as-made CNT/PVA | – | 1.3–1.5 ± 0.2 | 0.15 ^{a)} | 0.11 ^{a)} | 9–15. | 6–11 ^{a)} | [54] |
| HCl used for coagulation annealed at 1000 °C | – | – | – | 0.65 | | 12 | [55] |
| DNA dispersion, annealed (320–350 °C, 2 h) | – | – | 0.101 | – | 14.5 | – | [56] |
| hyaluronic acid used as dispersant and 0.3 M HNO ₃ as coagulant | – | – | 0.11 ± 0.003 | – | 13 ± 1 | – | [57] |
| dry spinning, directly from CVD reactor | | | | | | | |
| as-made | – | 1.7–2 ^{a)} | 0.4–1.25 | 0.2–0.75 | 34 ^{a)} | 20 ^{a)} | [61] |
| as-made | 0.03–0.1 | 0.4–1 | 0.5–1.5 | 0.5–1.5 | 50–150 | 50–150 | [2] |
| as-made (metallic CNTs) | 0.03–0.05 | – | – | – | – | – | [9] |
| oxidation (1 h, 400 °C, air), soaking (72 h, 30% H ₂ O ₂ and 24 h, 37% HCl) DI water wash, soaking (24 h, 98% H ₂ SO ₄) DI water wash | – | 0.28 | 0.32 | 1.14 ^{a)} | – | – | [7] |
| as above additionally I ₂ doping at 200 °C for 12 h | – | 0.33 | 0.64 | 1.94 ^{a)} | – | – | [7] |
| soaking with DI water, annealing at 200 °C | – | 1.8 | – | – | – | – | [79] |
| doped with KAuBr ₄ | – | 1.97 | – | – | – | – | |
| dry spinning, from CNT array | | | | | | | |
| as-spun (single yarn) | 0.01 | – | 0.15–0.30 | – | 4.5 ^{a)} | – | [4] |
| as-made | – | 0.8 | 0.55 | 0.69 ^{a)} | 20 | 25 ^{a)} | [71] |
| as-made | – | 0.8 | – | – | – | – | [72] |
| as-made | – | – | 0.85 | – | 275 | – | [64] |
| as-made, twisted | – | – | 1.91 | – | 300 | – | [64] |
| as-made arrays grown by water-assisted CVD | – | 0.9 | – | – | – | – | [70] |
| as-made, arrays grown by water-assisted CVD | – | – | 0.35 ± 0.07 | – | 25 ± 5 | – | [82] |
| as-made | 0.35–0.9 | 0.38–0.84 | – | 0.65 | – | 18 | [62,69] |
| as-made shrunk (and twisted) | – | 0.38–0.64 ^{a)} | 0.6–1.1 | 1.56–1.71 | 56 | 87 ^{a)} | [6] |

^{a)}Values inferred from the data provided by authors.

for the density of the material divided by density of water) as a normalizing factor even better values are obtained.^[2] Table 1 lists the mechanical properties of fibers characterized

electrically in Table 2. Where possible the specific strength and stiffness were found or calculated based on the data provided by the authors.

Table 2. Electrical and thermal properties of CNT fibers characterized mechanically in Table 1.

| Fiber treatment | Type of CNTs | length | diameter | Electrical properties of CNT fibers | | | | | Refs. |
|---|--------------|---------------------|--------------------------|-------------------------------------|--|----------------------------------|------------------|-----------------------|-------|
| | | | | σ | σ' | $J_{\max}^{(c)}$ | T_o | κ | |
| | | | | [S cm ⁻¹] | [S m ⁻¹ /g cm ⁻³] | [A cm ⁻²] | [K] | [W mK ⁻¹] | |
| electrospinning | | | | | | | | | |
| spun with PVB, annealed (400 °C) | MWNT | no limit | — | 154 ± 9.6 | 0.03 × 10 ⁶ a) | — | — | 5 | [49] |
| CNTs refluxed in 6N HNO ₃ for 24 h before spinning | SWNT | — | 0.2–5 | 355 | — | 10 ⁷ | — | — | [48] |
| wet-spun fibers from liquid crystalline phase | | | | | | | | | |
| annealed (280 °C 2 h) | MWNT | no limit | 10–80 | 80 | — | — | — | — | [53] |
| nitrogen doped CNTs | MWNT | no limit | 10–80 | 300 | — | — | — | — | [53] |
| 102% H ₂ SO ₄ doped | SWNT | no limit | tens of μm ^{a)} | 5000 | 0.5 × 10 ^{6a)} | — | — | 21 | [50] |
| vacuum anneal. 1100 °C 1 h | SWNT | no limit | tens of μm ^{a)} | 500 ^{a)} | — | — | — | — | [50] |
| spinning with the use of HSO ₃ Cl, H ₂ SO ₄ | SWNT | no limit | tens of μm ^{a)} | 8333 | — | — | — | — | [51] |
| 100% H ₂ SO ₄ (24 h, 100 °C) | SWNT | no limit | 60 | 4170 | — | — | 200 | 17 | [52] |
| annealed at >1000 °C | SWNT | no limit | 60 | 382 | — | — | >300 | — | [52] |
| doped with HSO ₃ Cl, | SWNT | no limit | 8–10 | 29 000 ± 3000 | 2.2 × 10 ⁶ a) | — | 60 | 380 ± 15 | [3] |
| doped with HSO ₃ Cl and I ₂ | SWNT | no limit | 8–10 | 50 000 ± 5000 | 4 × 10 ^{6a)} | — | 40 | 635 | [3] |
| doped as above – annealed at 600 °C in Ar and H ₂ | SWNT | no limit | 8–10 | 4000 | — | — | 200 | 635 | [3] |
| other wet spun fibers | | | | | | | | | |
| as-made CNT/PVA | SWNT | 100 | 2–100 | 10 | 0.07 × 10 ^{4a)} | — | — | — | [54] |
| spun with PVA annealed (1000 °C in H ₂) stretched | SWNT | — | — | 200 ^{a)} | — | — | >300 | 10 | [58] |
| HCl used for coagulation annealed at 1000 °C | SWNT | — | 10–50 | 140 | — | — | — | — | [55] |
| DNA dispersion, annealed (320—350 °C 2 h) | SWNT | 50 | 20–30 | 166.7 | — | — | — | — | [56] |
| hyaluronic acid used as dispersant and 0.3 M HNO ₃ as coagulant | SWNT | <1000 ^{a)} | tens of μm ^{a)} | 537 ± 56 | — | — | — | — | [57] |
| dry spinning, directly from CVD reactor | | | | | | | | | |
| as-made | SWNT | 20 | 50–500 | 1400 | — | — | 90 | — | [60] |
| as-made | DWNT | no limit | 10–200 | 5000 | 0.29 × 10 ^{6a)} | — | — | — | [61] |
| as-made | mixture | no limit | 10–20 | 3150 | 0.7 × 10 ⁶ | — | 85 | 1230 | [2] |
| as-made (metallic NTs) | SWNT | no limit | 10–20 | — | 2 × 10 ⁶ | — | 70 | — | [9] |
| oxidation (1 h, 400 °C, air) soaking (72 h, 30% H ₂ O ₂ and 24 h, 37% HCl), DI water wash, soaking (24 h, 98% H ₂ SO ₄), DI water wash | DWNT | — | 5.5 ^{a)} | 20 000 | 6 × 10 ⁶ | 10 ⁴ –10 ⁵ | — | — | [7] |
| as above additionally I ₂ doping at 200 °C for 12 h | DWNT | — | 4.1–44.7 | 11200 ^{b)} | 4 × 10 ^{6a)} | 10 ⁴ –10 ⁵ | — | — | [7] |
| | DWNT | — | 5.5 ^{a)} | 67 000 | 19.6 × 10 ⁶ | 10 ⁴ –10 ⁵ | 60 ^{a)} | — | [7] |
| | DWNT | — | 4.1–44.7 | 23 100 ^{b)} | 7 × 10 ^{6a)} | 10 ⁴ –10 ⁵ | 70 ^{a)} | — | [7] |
| soaking with DI water, annealing at 200 °C | — | — | 330 | 2970 ^{a)} | 0.16 × 10 ^{6a)} | — | >400 | — | [79] |
| doped with KAuBr ₄ | — | — | 330 | 13 000 | 0.66 × 10 ^{6a)} | — | <100 | — | [79] |
| dry spinning, from CNT array | | | | | | | | | |
| as-made (single yarn) | MWNT | no limit | 2–10 | 300 | — | — | >300 | — | [4] |
| as-made | MWNT | no limit | 10 | 300 | 0.037 × 10 ⁶ | 1.4 × 10 ⁴ | >360 | — | [71] |
| as-made | MWNT | no limit | 8.5–10 | 300 ^{a)} | 0.037 × 10 ^{6a)} | — | >300 | 26 | [72] |
| as-made | MWNT | no limit | 3 | 595.2 | — | — | >300 | - | [81] |
| annealed in air 480 °C | MWNT | no limit | 3 | 818.3 | — | — | >300 | — | [81] |
| oxidized in 5 N HNO ₃ | MWNT | no limit | 3 | 969 | — | — | >300 | — | [81] |
| as-made | MWNT | no limit | 4 | 170 | — | — | >300 | — | [64] |
| as-made, twisted | MWNT | no limit | 3 | 410 | — | — | >300 | — | [64] |

Table 2. Continued.

| Fiber treatment | Type of CNTs | length [cm] | diameter [μm] | Electrical properties of CNT fibers | | | | | Refs. |
|---|--------------|----------------|----------------------|-------------------------------------|--|-----------------------|-------|-----------------------|---------|
| | | | | σ | σ' | $J_{\max}^{c)}$ | T_0 | κ | |
| | | | | [S cm ⁻¹] | [S m ⁻¹ /g cm ⁻³] | [A cm ⁻²] | [K] | [W mK ⁻¹] | |
| as-made, arrays grown by water-assisted CVD | MWNT | no limit | 10–34 | 400–810 | 0.04–0.09 × 10 ^{6a)} | – | >300 | 20–78 | [70] |
| as-made, arrays grown by water-assisted CVD | MWNT | no limit | 12 × 5 ^{c)} | 500 | – | – | – | – | [82] |
| as-spun | MWNT | no limit | 12–27 | 150–370 | 0.045 × 10 ⁶ | – | – | – | [62,69] |
| as-spun shrunk (and twisted) | MWNT | no limit | 4–34 | 500–900 | 0.13–0.14 × 10 ^{6a)} | – | – | – | [6] |
| dry spinning, from CNT cotton | | | | | | | | | |
| oxidation (350 °C, 24 h), immersion (37% HCl, 48 h) | DWNT | 1 | 5–20 | 5900 | – | >10 ⁵ | – | – | [73] |

^{a)}Values inferred from the data provided by authors; ^{b)}Average value recorded for samples with wide range of diameters; ^{c)}Dimensions of rectangular cross-sectional area.

Figure 7a shows a comparison of the normalized strength and stiffness of the best CNT fibers from Table 1 and conductive metals. These fibers give an example that the specific strength and stiffness of fiber may be already at least several times better than any material used for conventional electrical engineering applications.

4.2.3. Thermal Properties of CNT Fibers

The thermal properties of CNT fibers have not received much attention so far. To the best of our knowledge, there are only two reports, at the time of writing, on thermal diffusivity and the heat capacity of CNT fibers. The thermal diffusivity amounted to 62 mm² s⁻¹ for MWNTs fiber drawn from the forest^[72] and 2.96 mm² s⁻¹ for annealed MWNT fiber electrospun with the aid of polymer.^[49] The heat capacity equalled 700 ± 50 J kg⁻¹ K⁻¹ and 4500 J kg⁻¹ K⁻¹ for forest spun^[72] and electrospun^[49] CNT fibers respectively. The first value is consistent with the heat capacity of graphite. However, the heat capacity of electrospun fibers is unexpectedly high, which may result from the presence of foreign substances present in the fiber.

A few authors have measured thermal conductivity. Most of the reported values (Table 2) range from 5–60 W m⁻¹ K⁻¹ for the axial direction, which is an extremely poor result compared to the values of axial thermal conductivity of individual nanotubes (see Section 2.3 for details). Such low values of axial thermal conductivity and diffusivity in CNT assemblies are mostly attributed to morphology issues including defects in the nanotubes, interconnections of CNT bundles, misalignment, and so forth. The recent experimental results of Behabtu et al. show that the CNT fibers doped with chlorosulfonic acid during spinning have approximately 10 times the thermal conductivity than that measured before of 380 ± 15 W m⁻¹ K⁻¹, and additionally doping can increase this to 635 W m⁻¹ K⁻¹, which is already much higher than that of metals used in electrical wiring.^[3] Moreover, theoretical calculations and experimental measurements of James et al. showed that a much higher value of axial thermal conductivity, that is, 1230 W m⁻¹ K⁻¹ should be expected from CNT fibers.^[80] This indicates further experimental and theoretical studies are necessary to understand this issue.

4.2.4. Electrical Properties of CNT Fibers

Electrical Conductivity: Currently, the preservation of the unique electrical properties of individual nanotubes in macroscopic carbon nanotubes assemblies turns out to be a challenging task. This is due to non-uniformity of produced nanotubes in terms of chirality, diameter, length and number of walls. Further, the conductivity of the macroscopic CNT structures is sensitive to defects of constituent CNTs (mentioned in Section 2.3), as well as to overall structural flaws like nanotubes misalignment, local entanglements or poor densification. Resistance is increased by impurities like amorphous carbon and aromatic hydrocarbons found on as-synthesized CNTs, which constitute additional scattering points for electrical transport. Therefore, the values of conductivity obtained in most CNT fibers (Table 2) are still not satisfactory in terms of electrical wiring applications.

At the moment the as-produced fibers have an extremely wide range of conductivities reported from 10 S cm⁻¹ to 67 000 S cm⁻¹.^[7,54] This is related to the quality of the as-made material but also to the presence of foreign molecules/chemical compounds in the fibers. Therefore, to obtain a reliable comparison of the true conductivity values reported by different authors it is highly important to consider all the pre- and post-processing treatments including purification steps or annealing time and temperature together with the overall conductivity value. For example, small diameter DWNT fibers spun directly from CVD reactor showed extremely high conductivity of 20 000 S cm⁻¹.^[7] However, purification steps applied included oxidation in air for 1 h at 400 °C, soaking for 72 h in 30% hydrogen peroxide, 24 h in 37% HCl, washing with DI water, and soaking in 98% sulfuric acid. Such harsh conditioning must have had a severe influence on the conductivity of these fibers. Similarly, the conductivity reported Behabtu et al. in the fibers annealed to 600 °C in Ar/H₂ atmosphere amounted to 4000 S cm⁻¹, which is extremely high for annealed fibers.^[3] The earlier papers of the same authors presented similar fibers annealed to at least 1000 °C in vacuum, which conductivities were an order of magnitude lower.^[50] Therefore it may be expected that annealing at 600 °C did not remove all the residual dopants.^[3]

The fibers may be also affected by ambient conditions. The basic studies on CNT powders showed that CNTs are generally

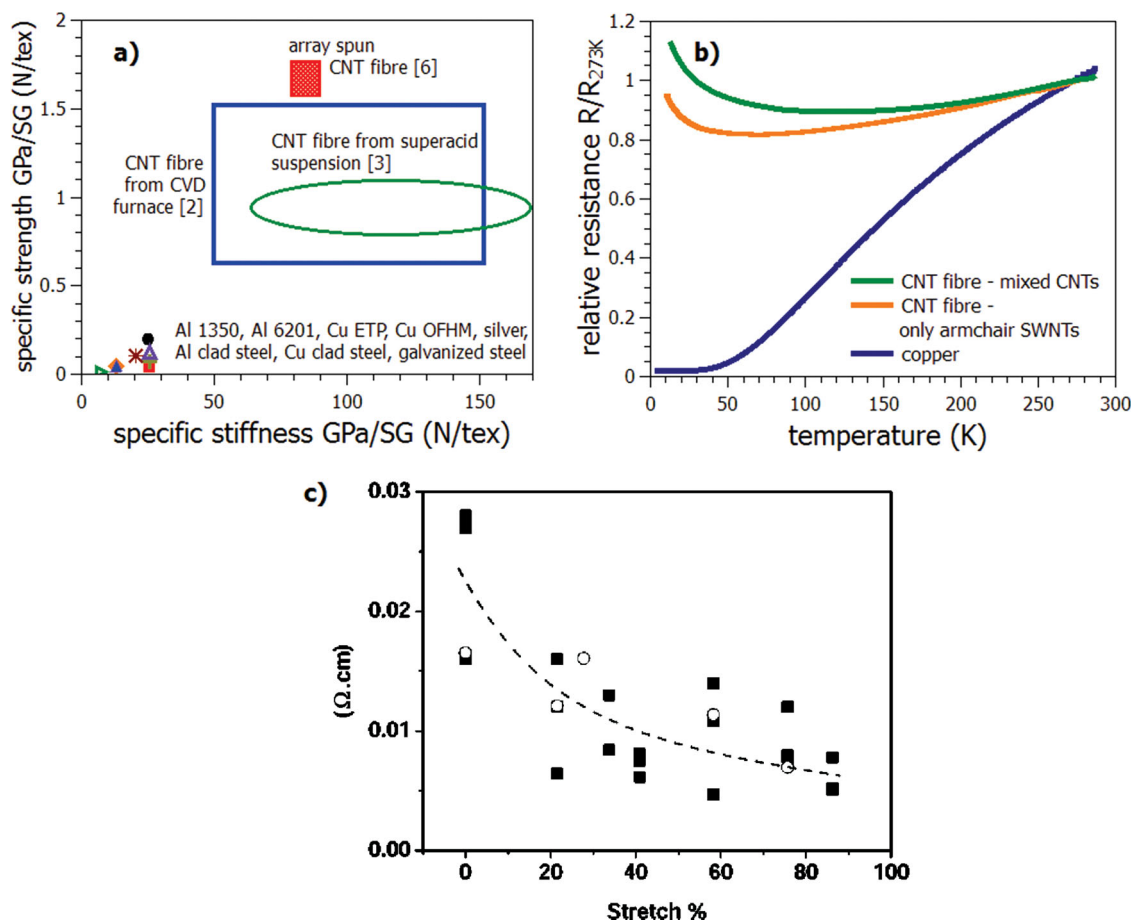


Figure 7. a) Mechanical properties of conventional conductors and chosen CNT fibers. Al 1350, Al 6201, Cu ETP, Cu OFHM, Al clad steel and Cu clad steel stand for Aluminium 1350 H19, Aluminium 6201 T81, Copper Electrolytic-Tough-Pitch, Copper, Oxygen-free high thermal conductivity, Aluminium clad steel and Copper clad steel respectively. b) Comparison of low temperature relative changes of electrical resistivity for copper (green line) and two CNT fibers spun directly from CVD reactor: standard CNT fiber (red line) and CNT fiber made purely of metallic SWNTs (blue line). Resistance related to the resistance of a given sample at 273 K. c) The decrease of resistivity of CNT fiber with stretch applied to it observed by Badaire et al. Reproduced with permission.^[72] Copyright 2012, American Institute of Physics.

sensitive to oxygen present in air.^[83] The adsorption of oxygen causes an increase in conductivity and strong p-doping of CNTs. Moreover, we recently found that air humidity has an impact on the electrical conduction of CVD grown as-made CNT fibers.^[84] The adsorbed molecular water causes an increase in the absolute conductivity of fibers. However, the increase is never as high as in case of strongly doping acids and the fibers may be further doped with, for example, hydrochloric or nitric acids. Although the adsorption of water does not influence the specific conductivity the ambient conditions of measurements should be definitely mentioned when comparing the absolute values of conductivity. Similarly as it is important to describe all the production and processing methods used for fiber manufacturing. Therefore, the conductivity values listed in Table 2 are accompanied by such information.

To obtain comparable results between fibers produced by various groups, it would be useful to introduce some standard procedures for conductivity measurements. Based on the analysis of the literature it is reasonable to suggest that the samples annealed at 500 °C in high vacuum of above 10^{-6} Torr for several hours should be free from most contaminants.

The use of high vacuum will assure that the air contaminants trapped in the material will be removed before they may cause oxidation of carbon nanotubes at high temperature, whereas, the temperature of 500 °C, at such high vacuum, should be enough to drive off all non-CNT materials from the fiber.

The as-made fibers spun with the aid of polymers have a very poor conductivity of up to 10 S cm^{-1} ^[54] as the molecules of polymer, which is an insulator, remain in the assembly impeding current transport through the fibers. The post-process annealing may improve the conductivity. The maximum conductivity obtained amounted to approximately 200 S cm^{-1} .^[58] The use of hydrochloric acid as coagulant improved the conductivity of as-made fibers to 140 S cm^{-1} .^[55] Similarly to wet spinning techniques, the electrical methods require the use of dispersants. Imaizumi et al. reported the conductivity of the fibers amounting to 154 S cm^{-1} after removal of polymer via annealing.^[49] The fiber electrospun with the use of sodium dodecylbenzenesulfonate reached the conductivity of 355 S cm^{-1} .^[48] However, in the spinning preparation process, the CNTs were treated with acids. Anyhow, the range of values obtained via these methods is still much too low for electrical wiring applications.

The electrical conductivity of fibers drawn from CNT forests reaches hundreds of S cm^{-1} .^[4,6,70,81] The values possible to obtain are higher than conductivities of the fibers spun via wet methods without acids, however, lower than the conductivities of fibers spun directly from CVD reactor. These fibers reached the conductivity of thousands of S cm^{-1} at ambient conditions.^[60,61,79] This is at least several times higher than most of fibers produced using other dry spinning methods and is in the range of the standard fibers spun from superacid liquid crystals.^[50–52] Up to now the highest absolute conductivity has been reached in very fine fibers from CVD furnace purified with the use of strong acids and doped with iodine. It amounted to $67\,000\text{ S cm}^{-1}$ which is an order of magnitude more than CVD grown and standard liquid crystalline spun fibers.^[3]

Specific Conductivity: Apart from the difficulties of the measurement of real electrical conductivity of pure CNT fibers described in previous subsection on electrical conductivity the calculation of resistivity based on the estimation of cross-sectional area of fibers is highly unreliable. This is due to the fact that the cross-sections of the fibers are often far from circular. Therefore many authors have proposed specific conductivity which uses linear density as a normalizing factor.^[7,8,62] The specific conductivity is calculated as:

$$\sigma' = \frac{GL}{LD} \times 10^9 \quad (1)$$

where: σ' is specific conductivity (in Siemens per meter over gram per cubic centimetre), G is conductance (in siemens), L is length (in meter) and LD is linear density (in tex). All the quantities required in Equation 1 can be found experimentally (see also Section 4.2.1). For standard conductors like copper, the specific conductivity will be simply the conductivity divided by volumetric density. Thus, the use of specific conductivity enables the reliable comparison of the electrical properties of widely used conducting materials. More importantly, it takes into account the volumetric density, which determines the weight of a final electrical device and is often crucial for the choice of a conductive material, particularly in aerospace applications or overhead power lines.

It has been reported that CNT yarns doped with iodine may reach the specific conductivity of $19.6 \times 10^6\text{ S m}^{-1}\text{ g}^{-1}\text{ cm}^3$, exceeding the specific conductivity of aluminium and copper, which amount to $14.15 \times 10^6\text{ S m}^{-1}\text{ g}^{-1}\text{ cm}^3$ and $6.52 \times 10^6\text{ S m}^{-1}\text{ g}^{-1}\text{ cm}^3$ for aluminium and copper, respectively.^[7] The values of specific conductivity reported for undoped material are still below copper which indicates that further optimization of the CNT fibers for conductivity is required.^[60,61,79] As described in Sections 2 and 3, based on the knowledge of the properties and behavior of individual CNTs and their assemblies, there is still a lot of room for improvement in this respect.

Resistivity Dependence on Temperature and Temperature Coefficient of Resistivity: Apart from the electrical resistivity (conductivity) at room temperature, an equally important parameter characterizing the electrical transport in the CNT fiber can be the dependence of its resistivity ρ on temperature T . Traditional metals decrease in resistivity with the lowering of

their temperature due to the reduced scattering of transported charges. This continues down to temperatures below approximately 30 K, where the resistivity maintains a small constant value originating from the intrinsic disorder of its structure. On the other hand, semiconductors have a virtually infinite resistivity close to 0 K and it decreases with increasing temperature due to the increase of the numbers of charge carriers and their mobility. Further, well above room temperature, scattering events overweigh this effect, turning the $d\rho/dT$ ratio from negative to positive.

However, the dependence of the resistivity of the currently produced CNT fibers on temperature differs from both metals and semiconductors. In general, the resistivity will drop with decreasing temperature down to a crossover temperature T_0 , below which it will start increasing, but, the T_0 may change over a very wide range of temperatures and the conductivity close to 0 K may vary from finite down to completely suppressed. For example, the crossover temperature for CNT fibers has been reported to vary from 40 K to well above room temperature (Table 2).^[3,52,79]

The theoretical explanation of this behavior is still debatable. The models used to fit the experimental data included variable range hopping, fluctuation assisted tunneling or weak/strong localization.^[3,85–87] However, none of the suggested models was initially developed to describe the electron transport through a macro-assembly of nanotubes and none of them is able to provide a universal mathematical description of the resistance changes of all the types of CNT fibers in the entire range of temperatures incorporating turnover from metallic to semiconducting-type behavior. Therefore, more work in this area is definitely necessary.

It has been observed that these changes in the features of the ρ – T curves are dependent on the morphology of the fibers. The characteristics of the structure which would be ideal for electrical wires, that is, higher share of metallic CNTs in the assembly, better purity, crystallinity, alignment and packing density of the CNTs as well as doping are resulting in more metal-like features of the resistance–temperature (R – T) curves.^[3,64,79,86–90] The upturn temperature for these materials will be low and the resistance will not increase considerably with decreasing temperature in the semiconducting part of the characteristic. Any deviation from such morphology as well the removal of dopants will result in the enhancement of semiconducting features of resistance temperature characteristics. Hence, the measurement of the resistance–temperature may be used as a helpful tool for an additional assessment of the quality and state (doped/undoped) of the produced material and its suitability for electrical wiring applications. As an example Figure 7b shows the R – T curve of a standard copper wire, CNT fiber made purely of armchair SWNTs and a standard fiber spun directly from CVD furnace with mixed types of nanotubes.

Another useful parameter related to resistivity–temperature dependence is the temperature coefficient of resistivity—a standard engineering parameter used to describe the stability of resistance of the material upon change in temperature. Often the resistivity–temperature dependence around room temperature may be simplified to a linear function and the temperature coefficient of resistivity— α is found as the gradient of this function, measured in units of K^{-1} . For electrical wiring applications the absolute value of α should be as low as possible, as it ensures

insensitivity of the conduction of the wire to changing temperature conditions. As shown in Figure 7b the slopes of resistivity-temperature characteristics below room temperature for both presented CNT fibers are much smaller than for copper. Based on the available reports the α coefficients of CNT fibers around room temperature vary from -0.001 K^{-1} to 0.002 K^{-1} ,^[3,4,7,71,72] that is, the absolute values are approximately half those of copper and aluminium, which is a very promising result.

Maximum Current Density: As mentioned in Section 2.3, the maximum current density (10^9 – 10^{10} A cm^{-2}) measured for individual carbon nanotubes at room temperature, is considerably higher than maximum current density of copper wires and even higher than maximum critical current densities of superconductors.^[26–28] The maximum current densities measured at ambient conditions for most CNT fibers are substantially lower and amount to 10^4 – 10^5 A cm^{-2} .^[7,71,73] This value is nonetheless a very good result considering the fact that the current densities used in real applications are much smaller.^[91] As an example the current density in insulated copper wiring used in domestic devices working in constant duty cycle amounts to 200 – 400 A cm^{-2} and in intermittent duty cycle to 1000 A cm^{-2} , maximum admissible current density allowed for one second in non-insulated copper, aluminium and steel wires in normal operating conditions equals 15 – 900 A cm^{-2} , $10\,500\text{ A cm}^{-2}$, and 5800 A cm^{-2} respectively, while the average engineering current density (minimum amperage 90 A, operation below 90 K) of type 344C—copper stabilized YBCO 2G HTS wire amounts to $10\,200\text{ A cm}^{-2}$.^[91,92]

The maximum current that may be transported through a wire without any damage to the fiber which is also referred to as current carrying capacity is related to the electrical resistivity of the material, frequency of the current and efficiency of heat removal controlled by the magnitude of surface area available for heat dissipation and external factors such as ambient temperature or insulation. This suggests that the improvement of electrical conductivity of the CNT fibers should further increase their current carrying capacity. On the other hand, better condensation of the fibers, which is one of the possible methods of improving the conductivity, will decrease the porosity and thus the surface area available for heat removal which will not be beneficial for current carrying capacity. Therefore, more studies on this issue are necessary.

High Frequency Signals in CNT Fibers: Transport of high frequency signals through conventional conductors is a problematic task mainly due to skin and proximity effects. Skin effect is a phenomenon observed in bulk conductors, at higher frequencies, where the current density is largest near the surface of the conductor. This causes a decrease of the cross-sectional area available for charge transport and increases the effective resistance. The proximity effect leads to similar inefficiencies as a result of the electromagnetic interaction between wires in close proximity.

It is expected that the nanoscale tubular and fibrous nature of CNTs should mitigate both the skin and proximity effects and enable a high frequency transport superior to typical metals.^[93,94] Moreover, with every resistive CNT to CNT junction, there also exists a parallel CNT to CNT capacitance that, for a sufficiently high frequency current, effectively shorts out the resistive junction of the charge carrier's pathway.

Considering that junction resistance dominates the overall textile conductivity, above a certain frequency, overall textile conductivity should increase—the opposite the behavior of metals.

This area of CNT high frequency transport still needs further exploration. A few experimental studies have indicated trends, but these are not totally conclusive. For example, Xu et al.^[94] explored the conductivity of SWCNT films from 10 MHz to 30 GHz. The conductivity began increasing at 100 MHz, with a significant enhancement around at 10 GHz. By 30 GHz, the conductivity nearly doubled, without any indication of saturation. While these are CNT films and not fibers, high frequency measurement often requires films to extract a frequency dependent conductivity, but the bulk material results may be applied to the fibers. Jarosz et al.^[95] fabricated a functional CNT coaxial cable where the inner and outer conductors were made from bulk CNT textiles. They found the high frequency (up to 3 GHz) performance of the cable increased after doping treatment with KAuBr_4 . However, copper still outperformed every variation of their CNT coaxial cable. This indicates that better understanding of the material is still necessary and more studies on these issues are required.

4.2.5. CNT fibers in Harsh Conditions

The systematic studies of Janas et al. showed that CNT fibers are highly resistant to harsh chemical conditions, where copper wires get severely corroded.^[96] The comparative immersion tests performed over 30 days showed that CNT fiber has not been damaged by any of the tested liquids which included concentrated nitric acid, hydrochloric acid, and sulfuric acid as well as saturated sodium chloride solution (to model sea water) and deionized water. The resistance of the fibers first slightly decreased due to doping effects and then quickly stabilized. The copper wire got completely dissolved in acids, while salty and deionized water caused the corrosion of the surface layer and thus the rapid increase in resistance and then its stabilization. These tests indicate that the CNT fibers may replace copper in the environment where copper wires get damaged or completely destroyed.

The tests performed on the CNT fibers at very high temperatures, in air, showed that the performance was as expected for carbon materials of this type and the fibers operated well up to approximately $450\text{ }^\circ\text{C}$ and then degraded rapidly.^[97] This should be sufficient for most electrical wiring applications however it was also shown that if necessary the application of a passivating layer of silicone carbide may increase the safe operational window up to $700\text{ }^\circ\text{C}$.

5. Optimization of CNT Fiber Properties for Electrical Wiring Applications

Table 3 provides a comparison of the currently produced CNT wires and traditional copper wires. From this it can be seen that in terms of costs, fabrication and maintenance the CNT wires have an advantage over the copper wires. However, the

Table 3. Brief comparison between CNT wires (properties cited from Tables 1, 2) and traditional copper wires.

| | | CNT wires | copper wires |
|-----------------------|---|---|-------------------------------|
| costs | production | low | high |
| | maintenance | low | low |
| fabrication/recycling | availability of resources | abundant | limited |
| | complexity of processing | low | high |
| | environmental impact | minimal | high |
| | recycling | good | good |
| maintenance | working life in normal operating conditions | long | long |
| | corrosion resistance | high | low |
| | temperature stability in oxygen atmosphere | low | medium |
| | temperature stability in inert atmosphere | high | medium |
| properties | density [g cm^{-3}] | 0.28–2 | 8.9 |
| | electrical conductivity [S cm^{-1}] | 10–67 000 | 580 000 |
| | specific electrical conductivity [$\text{S m}^{-1}/\text{g cm}^{-3}$] | 0.07×10^4 – 19.6×10^6 | 6.5×10^6 |
| | current carrying capacity [S cm^{-2}] | 10^4 – 10^7 | 3×10^4 ^{a)} |
| | tensile strength [GPa] | 0.013–1.91 | 0.220 |
| | specific tensile strength [GPa SG ⁻¹] or [N tex ⁻¹] | 0.027–1.94 | 0.025 |
| | axial thermal conductivity [W mK^{-1}] | 5–1230 | 400 |

^{a)}Copper wire of tens of mm in diameter; current flowing for 1 s in air at room temperature.^[98]

state of the art electrical performance of CNT fibers, although very promising, is still not sufficient for most electrical wiring applications. Considering the properties of individual CNTs and all theoretical predictions it should be possible to obtain much better properties from the fibers, however this is conditional on the prerequisite that the morphology of the fibers can be well controlled. The following section recognises all the imperfections of the structure of currently produced fibers which cause the deterioration of the electrical properties of the fibers. It also describes all the solutions which have been introduced so far and suggests some possible steps for the future, based on the state of the art knowledge of individual CNTs and CNT assemblies.

5.1. Type of Nanotubes

The first factor influencing electrical performance of the CNT based fibers is the type of CNTs present in the structure. For the best electrical conductivity the fiber should consist solely of one type of small diameter armchair SWNTs. The use of armchair CNTs will ensure the highest possible conductivity, as only these nanotubes are truly metallic independent of their diameter.^[14,15] The small diameter of nanotubes will guarantee very good packing of the structure and minimal volume of the conductor. Finally, according to theoretical calculations the use of one type of nanotubes (which are mirror images of each other) will ensure the best electronic coupling between the nanotubes in a rope.^[99,100]

The preference for a SWNT over MWNT based fiber may be explained by the theoretical studies which show that even if MWNT comprises only armchair shells (which theoretically may exist but practically are difficult to synthesize), some electronic distortions may be expected depending on the mutual

arrangements of the lattices.^[101] The experiments of Bourlon et al. performed on MWNTs with shells of random chiralities showed that at low bias, only outermost shells contribute to the overall conduction, as the internal shells are not physically attached to the electrodes.^[102] Only for large bias, all the shells were found to transport electrons.^[103] Based on the above cited theoretical and experimental studies it may be argued that even in case of purely armchair MWNTs the internal shells will not form a physical contact with other nanotubes in the fiber and therefore it may be difficult to ensure perfect electronic coupling between the inner and outer shells even if all of them are armchair.

The above condition of using only SWNTs may be an obstacle for two-step dry spinning methods as to the best of our knowledge none of the authors has yet shown that SWNT assemblies are spinnable. On the other hand, the production of purely SWNTs fibers was demonstrated both in case of wet spinning techniques and electrospinning (Table 3).^[48,50,54] These spinning methods have not yet been proved suitable for production of all armchair fibers, although potentially they may. This is due to the fact that the control of the chirality of nanotubes is still a highly challenging problem and commercially available material is always a mixture of nanotubes with random chiralities, which is expected to comprise only one third of metallic nanotubes.^[16] The potential separation of only armchair nanotubes from the mixture using the available techniques such as density-gradient ultracentrifugation or column chromatography^[104,105] is absolutely not an industrially viable process. Therefore, further development of the wet spinning and electrospinning techniques is at the moment highly dependent on the progress of the basic research on the chirality control of the nanotubes.

The solution to this highly challenging issue has been approached only in case of direct spinning from CVD reactor.^[9]

It has been shown that the proper control over the growth of catalyst, results in the synthesis of nanotubes of preferred diameter which corresponds to the required chirality. This result is highly promising as it proves for the first time that the production of fibers made purely of armchair SWNTs in indeed possible and industrially viable.

5.2. Length of Nanotubes

Considering the ideal case scenario that the CNT fiber comprises only type of armchair SWNT it is still necessary to consider the role of junctions in the electron transport over the whole fiber. The recent calculations of Xu et al. show that for precisely chosen length of the contact between same armchair SWNTs the electrons should be transferred without resistance and all the structure should behave as one long CNT.^[5] The authors argue that for practical purposes one should rather consider the production of very long contacts between nanotubes. This should be enough to approach the conductivity of one nanotube. Any resistance which arises from a non-ideal contact length may be mitigated by a tiny bias applied to the fiber. This indicates that to provide long enough contacts the nanotubes themselves should be as long as possible. Moreover, the increased length of the nanotubes within the fiber will also ensure a smaller number nanotube to nanotube contacts during the passage of a charge along the fiber. It was already shown that even in case of fibers made of various types of nanotubes the increase in length of the CNTs in the CNT fiber improves its electrical conductivity.^[81] Up to now, the best control over the length of CNTs in the fibers was obtained in the fibers spun from CNT arrays. Here, the length of the nanotubes is defined by the height of CNT array and this may be controlled the optimization of the production process such as the increase in the time of growth or addition of H₂O.^[81,106] Up to now, the record nanotubes used for spinning were 6 mm-long.^[107]

The materials prepared from floating catalyst CVD method contain slightly shorter but still quite long nanotubes. The CNT cottons were reported to contain up to 3 mm long CNTs.^[45] Whereas, the nanotubes of approximately 1 mm were found in CNT fibers directly spun from CVD furnace.^[2] However, up to now little is known about the parameters which control the length of nanotubes in the floating catalyst CVD process and further research on this issue is necessary.

The wet and electro-spinning techniques have up until now been restricted to the use of commercially available CNT powders mostly from HiPCO process, which contain very short nanotubes of several micrometres in length.^[108] However, regardless of the poor availability of longer nanotubes on the market, the processing of longer nanotubes in these spinning methods may impose some difficulties. Firstly, longer nanotubes may block the extrusion orifice if they are not well aligned and the use of liquid crystalline phase where the nanotubes get pre-aligned, may not be helpful either, as it has been pointed out that longer nanotubes are much more difficult to disperse in superacids.^[3,59] Although the recent paper of Parra-Vasquez et al. reported the dissolution of 0.5 mm long nanotubes.^[59] However, to the best of our knowledge, the spinning

with such nanotubes has not yet been reported. It is possible that wet spinning methods may need to be aided with other aligning techniques for example with electrical or magnetic fields.^[109]

5.3. Defects and Disorders of CNTs

As outlined in the Section 2.3 although defects may change the conductive properties of CNTs, armchair nanotubes, which would be the most suitable for CNT wires, are the least sensitive to defects. The formation of crystallographic defects such as vacancies which are the most harmful to armchair CNTs may be avoided by the increase of synthesis temperature.^[110] Better, material graphitization may be also obtained by postproduction annealing above 1900 °C in argon atmosphere.^[110,111]

Other disorders such as small radial compression or bending of the armchair nanotubes is not expected to cause any electronic changes.^[112] Unless, the nanotube is fully collapsed.^[113] Collapsing which appears naturally in SWNTs with the diameters above 2.5–3 nm should, however, be absent from small diameter nanotubes ideal for CNT wires.^[114]

The general misshaping of nanotubes may also introduce disorder into the whole CNT fiber structure and impede the proper condensation of the material. This problem has not been much observed in the wet and electro-spun fibers as they use extremely short nanotubes which are quite straight.^[3] In case of CNT arrays the misshaping of nanotubes has been addressed by the control of the catalyst and growth conditions during synthesis of the arrays.^[74] However, this issue has not yet been solved in the materials produced via floating catalyst CVD and further research in this area is necessary.

5.4. Packing of Nanotubes in the Fibers

As mentioned in Section 5.2 long contacts between nanotubes may assure almost resistanceless transport of charges between nanotubes and thus very high conductivity of the fibers. However, contacts that are long enough may be obtained if the CNTs themselves are long but also if they are close together, that is, the fiber is well condensed. The proper condensation also ensures good stress transfer and thus high mechanical strength of the fiber.^[2,78] Finally, lack of voids in the structure ensures the minimum volume of the conductor.

The wet spun fibers are normally condensed during coagulation and, further, upon room temperature evaporation or annealing of the remaining dispersant and coagulant.^[3] The wet spun fibers are normally quite well condensed, which also stems from the fact that only short straight nanotubes are used for spinning and their condensation is easier than in case of long nanotubes. The condensation process may improve or deteriorate the electrical properties of the final fibers depending on the interaction of the dispersant/coagulant with carbon nanotubes or its intrinsic electrical properties.^[50,78]

Most dry spun fibers as well as electrospun fiber reported by Imaizumi et al. were condensed via mechanical twisting.^[4,49,62,64,73] The systematic studies of Miao^[62] performed on the array spun twisted fibers showed that apart from

decreasing the volume of fibers and therefore absolute conductivity, twisting is not improving specific conductivity of fibers. This indicates that it is not increasing the number of connections in the network. Similar conclusion may be drawn from the results obtained by Zhang et al. as the twisting of fibers only slightly changed the low temperature behavior of the fibers towards less semiconducting.^[64] Finally, it was also shown that above a certain twisting threshold the mechanical properties of the fiber start to deteriorate due to the pull-out of the CNT bundles.^[78]

Another well-established method of densification of dry spun fibers is via spraying of organic solvents such as acetone, which wets CNT bundles and pulls them together upon evaporation.^[2] Densification with the use of liquids was found to improve the mechanical performance of the fibers.^[2] However, there were no detailed studies on the influence of this type condensation on the electrical properties. There is also no data available about the influence of another liquid densification route tested on dry and electrospun fibers. This method involves immersion in liquids which induce the condensation of the fibers due to the hydrophobic effect or surface tension forces exerted on their lateral surface.^[4,47,61]

There has been a report of drawing of the fibers through a die which is similar to drawing of wires out of ductile metal.^[79] This type of densification was found to improve the electrical conductivity in a wide range of temperatures. However, it may be expected that this type of densification may damage the surface of the fibers.

5.5. Anisotropy of CNTs and Their Alignment in the Fiber

CNTs are highly anisotropic structures. Their conductivity is the highest along the axial direction and considerably lower across the nanotube.^[12] Therefore to obtain the shortest pathway for the flow of charge and thus the best conductivity in the fiber all the nanotubes should be perfectly axially aligned. The ideal alignment will also ensure long contact areas mentioned in previous sections and thus decrease the overall resistance of the fibers.

In all the dry spinning methods the first alignment of nanotubes/nanotube bundles is defined during initial drawing of the fibers. The right balance between Van der Waals forces holding CNT bundles together and tensile forces aligns the CNT bundles axially.^[2,46,75,76] As shown by Koziol et al. this initial alignment (as well as densification) may be further improved by applying additional drawing to the fibers condensed via high vapor pressure liquid route.^[2] X-ray diffraction analysis indicates a misalignment of less than 10° in such doubly drawn fibers and improvement of their mechanical and electrical performance.^[2,115]

Similar drawing approach was also combined with twisting densification.^[58] However, it is quite difficult to assess its impact on alignment and thus electrical performance as in principle twisting as such introduces torsional misalignment which unnecessarily elongates the pathway for the electrons transfer along the length of the fibers, so is not ideal for obtaining the highest electrical conductivity.

The initial partial alignment of the fibers spun from liquid crystalline phase is obtained in the dispersion. Further

alignment is defined during the extrusion and coagulation.^[53] It was found that the degree of alignment is dependent on the die used for drawing the fiber. Increase in the die size results in higher misalignment and decrease in conductivity.^[52] In all other wet methods of CNT fiber production the first alignment is obtained during extrusion. The XRD analysis conducted by Badaire et al. showed the degree of misalignment of as-made fibers spun with the use of polymer is quite high and amounted to 27.5°.^[58] The misalignment may be decreased to 14.5° via post-spinning stretching by 80%, which results in a 4 times decrease in resistivity (Figure 7c). This observation applied both to as-made fibers as well as polymer free annealed fibers.

The fibers electrospun from surfactant stabilized suspensions take advantage of the surface tension of the suspension out of which they are withdrawn.^[47] The pre-alignment may be also obtained by applying an AC electric field before precipitation.^[48] Fibers electrospun with the use of polymer are aligned during extrusion and drawing/winding on the rotating collector.^[49]

5.6. Improvement of Conductivity with Chemical Methods

Many authors have shown that the conductivity of CNT fibers may be influenced by chemical treatment. Some of the chemicals cause an increase in conductivity and some a decrease. These effects are mostly attributed to doping, although in case of some compounds this explanation may be still ambiguous.^[3,7,52,79,116,117] The largest increase in conductivity of the CNT materials has been found for inorganic compounds including chlorosulphonic acid and nitric acid as well as chemical elements such as bromine, potassium and iodine.^[3,7,117] All these treatments make also fibers much more metallic in terms of resistivity-temperature dependence.^[3,85]

The largest increase in conductivity at the time of writing has been reported for multistep treated fibers. The highest specific conductivity exceeding copper and aluminium was obtained in the fibers spun from floating catalyst CVD after combined oxidative treatments, doping with hydrochloric and sulphuric acid and iodine.^[7] The best absolute conductivity was obtained in the fibers spun from chlorosulfonic acid liquid crystals, further doped with iodine.^[3] These are very interesting results showing the potential of the fibers for engineering of their properties. However, as mentioned in the introduction it would be much more desirable to obtain full control over the quality of the produced fibers as such harsh treatment of the fibers will severely increase the cost of production of wires and the treated fibers may not be suitable for all types of applications.

5.7. Impurities

The use of wet spinning methods for CNT fibers production results in the presence of many residual molecules of surfactant and coagulant in the final product. Particularly harmful for electrical properties are insulating polymers, which considerably decrease the electrical conductivity of CNT fibers. Most authors apply annealing to remove the non-conducting

molecules and thus improve the electrical performance of CNT fibers.^[49,53,56]

However, the mere synthesis of CNTs with any method results in the production of side materials including catalyst particles, various kinds of graphitic materials such as graphene, buckyballs, bamboo-shaped nanotubes, amorphous carbon, aromatic hydrocarbons etc.^[46,56,68] The insulating by-products may become obstacles for charge transport through the CNT network and decrease both absolute and specific conductivities. Moreover, the conductive but non-nanotube structures and compounds may add weight thus deteriorating the specific conductivity of the fibers.^[79] The impurities may also deteriorate the spinnability of the CNT forests.^[68] The widely-used methods of post-production removal of impurities include sonication in acid or annealing.^[89,110] Sonication increases the defectiveness of CNTs therefore annealing would be a preferred method. As shown by Koziol et al. annealing to 800 K in argon atmosphere removes most of the impurities from CVD fibers.^[110] However, the most efficient method of producing clean fibers would be the reduction in the amount of synthesised by-products already within the process. This may be obtained by the proper choice of feedstock.^[9,68,99]

6. Engineering Aspects of CNT Wires Development

The engineering aspects in CNT wire manufacturing are just as important as the optimization of CNT fiber properties described above. CNT fibers differ from conventional wiring materials based on metals. Therefore, all the steps of preparation of wires need some revision if CNT fibers are to be applied as the conductors. The main aspects to be considered include, first, the fast production of wires with the desired dimensions. Next, the fibers have to be provided with a suitable electrical insulation, using low-cost easy to scale up methods. Finally, the wires need to be connected to other live parts of electrical circuits with reliable, low-resistance and easy to apply electrical connections.

6.1. The Dimensions of the Wire

To consider a large scale production of CNT wires, first, the fibers of desired lengths and cross-sectional areas have to be produced with high speed. Although, the measurement of cross-sectional area of the fibers is quite unreliable and probably needs to be replaced by linear density in the future, to give a rough idea about the dimension of the produced fibers, we will further assume the fibers have circular cross-sections and compare their approximate diameters reported by the authors.

Regarding the length of produced CNT fibers the most viable industrially processes include direct spinning from CVD furnace, spinning from liquid crystalline phase and from CNT arrays. Dry direct spinning from CVD furnace allows the continuous production (unlimited length) of CNT fibers with the speeds up to 100 m min⁻¹.^[2,46,61] The diameters may be controlled from 1 μ m to several tens of micrometres (Table 2). If necessary, higher diameters may be obtained

by simultaneous spinning and joint condensation of several fibers. Such approach has been already demonstrated to work successfully for both liquid crystalline phase spinning and drawing from CNT arrays.^[3,118] In the former method several fibers of 8–10 μ m diameter were spun simultaneously at the speed of 10 m min⁻¹, which are probably the optimum parameters for this type of spinning. As mentioned in Section 5.5 the increase of extrusion orifice and thus the diameter had been found earlier to decrease the alignment of nanotubes and worsen the electrical conductivity, therefore small diameters should ideally be kept.^[52] The speed of 10 m min⁻¹^[3] is already high as for wet spinning process and definitely acceptable for large scale production. As reported by Ghemes et al.^[119] the spinning from CNT arrays may offer much higher drawing speeds of up to 600 m min⁻¹ (definitely to be slightly slowed down by adding the condensation step) and as according to other authors very wide range of fiber diameters from 1 μ m to tens of micrometres (Table 2).^[4,70] As mentioned above these fibers may be also drawn simultaneously from two different places on the array.^[118] However, some difficulties may be expected with regard to full automation of the process particularly when considering the pull out of the first bunch of CNTs and possible fractures of the fibers as a result of any defects in the array.

An interesting process which also offers the possibility of continuous production of fibers without a length restriction is the electrospinning proposed by Imaizumi et al.^[49] The collected on a rotating winder with the speed of 700 m min⁻¹ (which may indicate quite fast spinning of fibers) and had 350 μ m before removal of PVB (no data after removal). It may be expected that similarly to wet spun fibers the diameter of the fiber could be controlled by the size of the orifice and flow conditions.^[54] However, at the moment the conductivity of the fibers is very low and the method would need to be tested using some other CNT dispersions. It is possible that it would improve the scalability of wet spinning methods, which often may suffer from discontinuity and speed limitations. To the best of our knowledge, the most successful spinning was reported by Dalton et al.—meters-long fibers were spun at the speed 70 cm min⁻¹.^[120]

Other reported methods of fiber production which included spinning of fibers from CNT cottons,^[65,73] CNT films^[66,79] and withdrawing of the fiber from CNT dispersion using electrical methods^[47] enable the spinning of at most centimetres-long fibers, so at the moment are not suitable for large scale production of electrical wires. It may be expected that the CNT cotton and CNT film spinning will be very difficult to scale up due to high non-uniformity of the base materials, which will be quite difficult to control. The authors of electrospinning method tried to introduce some modifications to the spinning process and claimed the increase of the length of produced fibers however, no exemplary number was quoted.^[48]

6.2. Electrical Insulation

Electrical insulation is an essential part of many conventional electrical wires. It ensures that the current flows only along the designated pathways in the wire and prevents short-circuits with other live parts of the system or external objects as well

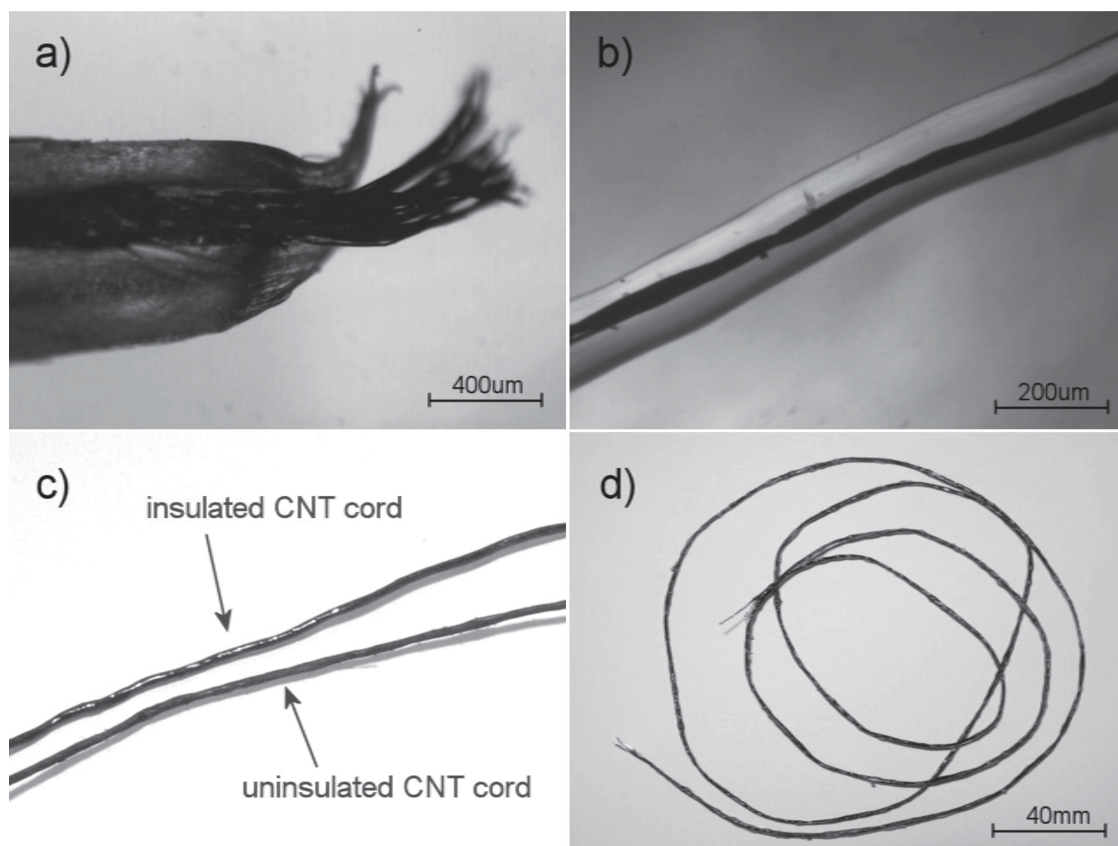


Figure 8. a) CNT cord insulated with low density polyethylene. Sample crosscut diagonally to show lack of infiltration of the insulation into the CNT fiber (optical microscope image). b) Optical microscope image of a thin CNT cord insulated with rubber compound. c) Comparison of thick insulated and uninsulated CNT cord. d) 1 metre-long insulated CNT cord.

as protects humans from electric shock. Additionally, insulation may help to prevent or reduce corrosion of the conducting wire.

Providing CNT fibers or cords with electrical insulation may be difficult due to extremely high porosity of these structures. On a laboratory scale this issue may be easily solved by threading the fiber through a ready-made insulating pipe as shown by, for example, Jarosz et al.^[95] or by using a heat shrink. However, this method will be restricted to very short lengths of the fibers and small scale applications. The best solution would be to use standard methods of insulation used in industry for continuous insulation of metallic cables such as extrusion of polymer or dip coating. Both of these methods require the use of liquid polymers which are later set by cooling or heating. However, the liquid polymeric compound may infiltrate the highly porous fibers resulting in the formation of a composite. Thus, the continuous conductive network of CNT bundles will be destroyed, which will result in a severe deterioration of electrical, mechanical and thermal properties of the fibers.

To address this issue we explored several parameters which may influence the infiltration of the liquid polymers into fibers and found out that the CNT fibers may be successfully insulated using polymers of high viscosity or liquid polymers which cannot wet CNT fibers due to hydrophobicity effect.^[8] We found that the condensed CVD grown fibers will not be infiltrated by the polymers of viscosity above 100 000 mPa s. This criterion

includes for example low density polyethylene (LDPE) used for the insulation of standard wires using extrusion method. **Figure 8a** shows the optical microscope image of CNT cord insulated with LDPE.

Moreover, the strong hydrophobicity of carbon nanotubes does not allow the wetting of CNT assemblies with a solution of polymers in water such as rubber latex. Rubber latex is a low viscosity liquid which sets thermally within seconds and may be applied to the fibers by dip coating. **Figure 9b–d** shows that latex remains on the surface of CNT fiber forming a thin, continuous and uniform insulation layer.

The above presented insulation methods may ensure low cost of insulation of the CNT fibers and can be very easily added to the CNT fiber production process thus forming a single production line of CNT wires.

6.3. Electrical Connections

Another issue determining the applicability of CNT wires in electrical circuitry are electrical connections, which need to provide a low-resistance, mechanically strong connection to other parts of the circuit. The connecting method needs to be simple, reliable and cost-efficient.

Although much has been done in the area of connecting individual nanotubes and small assemblies of nanotubes

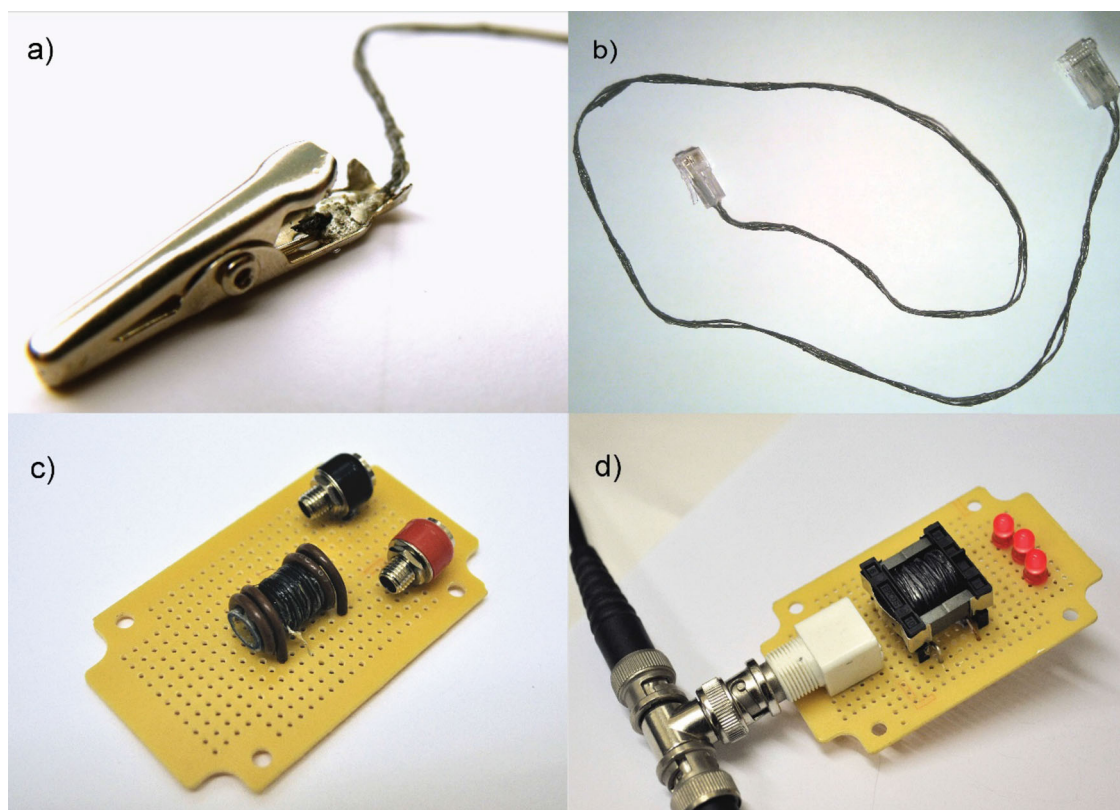


Figure 9. a) CNT wire with soldered to standard crocodile clips with the use of new carbon alloy. b) Ethernet cable produced using CNT wires. c) A coil wound using CNT wires on non-magnetic core. d) Demonstration of transformer with copper wiring replaced with CNT wires.

most of the methods, such as focused ion beam lithography^[27] are not applicable to macroscopic CNT fibers. The difficulty in providing an efficient electrical connection results from the fact that carbon materials are not easily wetted by metals. In case of electrical graphite this problem was solved by very high temperature (approx. 800 °C) joining called brazing. During brazing the surface of graphite is partly damaged by the formation of an interlayer of poorly conductive carbides between the metal and connected graphite. Apart from the high temperature issue the formation of non-conducting layer in the connection is not acceptable. To overcome all the above challenges, some other joining methods have been proposed.

The most commonly used laboratory method of connecting CNTs is the use of silver paint^[48,49] which is a suspension of nanoparticles of silver in organic solvent. The organic solvent wets the nanotubes allowing the deposition of silver particles on the CNT bundles and after evaporation provides low resistance electrical connection. The drawback of this connection is poor mechanical performance and tendency to oxidation.

It was also demonstrated that ultrasonic bonding may be used to provide a strong and fairly low resistance contacts. However, such a method is probably not applicable on a large industrial scale due to its complexity.^[121]

Electrical crimping is a method widely used to join conventional wires and may be used to join CNT fibers. The yarn structure of CNT fibers facilitates reshaping of the CNT fiber under pressure which increases the contact area between the

fiber and the pressing metal plates. It was also reported that deposition of a metal on CNT fiber may help to decrease contact resistance.^[121]

Another highly promising method is the use of carbon solder recently developed in our laboratory. Carbon solder may be applied using standard soldering iron. The temperatures used for soldering are in the range of 350–450 °C. The solder uses easily available metals excluding toxic lead. The solder may be used to join CNT fibers together as well as to any type of metal or graphitic material.^[10] It provides low-resistance joints of very high mechanical performance.

All the above techniques offer the same wide spectrum of simple low-cost joining techniques as in case of standard wires.

7. Examples of Electrical Wires and Electrical Devices Based on CNT Fibers

To demonstrate that CNT fibers may be successfully used as conductors a standard electrical wire, Ethernet cable, a coil and an electrical machine were produced. Figure 9a shows insulated CNT wire connected to crocodile clips where the joint is made with carbon solder. Such a wire can be used to light up a bulb as already demonstrated by many authors for bare as-made CNT fibers.^[3,7] Figure 9b presents an operating Ethernet cable which was successfully used to send data with the transfer speed of 10 MB s⁻¹. The insulated wires may be also used to wind up a coil.^[115] Figure 9c shows a 10-turns coil wound on

a non-magnetic core. The simple tests of the coil showed that the magnetic field was increasing linearly with applied voltage and reached approximately 100 μT for 9 V applied to the coil at 50 Hz. The parameters obtained in the CNT coil may be adjusted using standard techniques such as change of the amount of turns, shape of the coil or introduction of magnetic core.

The work on the development of CNT wires/coils paved the way to building of the working prototype of an electrical machine—a transformer.^[11] The transformers are widely applied machines used in all types of electrical systems. The potential substitution of conventional wires with CNT wires could be highly beneficial for applications where the weight and/or high frequency performance is of paramount importance such as in the aviation industry or audio/radio applications. For example the transformers used in aeroplanes are designed to work at increased frequency of 400 Hz. This feature, although making the integration of the transformers more difficult as they are incompatible with standard mains frequency of 50 Hz, enables the considerable decrease in the weight of these machines as it allows the use of less core material and windings. The increase of frequency entails the intensification of losses in the cores as well as skin and proximity effects in the wires which decrease the effective cross-sectional area available for current transport in the windings. Therefore, the use of CNT wires could possibly improve the performance of such machines.

We have recently shown that CNT wires may successfully replace copper wiring in an electrical transformer. Figure 9d shows the photo of the transformer in operation. The 21 and 12 turns of CNT windings were wound on the middle part of the triple column ferrite core. For testing purposes a 12-turns coil of copper was also placed close to the CNT windings. The transformer was tested up to 1 MHz which was the operational limit for the core. The results of open-circuit, load and short-circuit experiments were in agreement with the classical theory of transformers. The experiments showed that the high resistance of currently used CNT wires is an issue which needs to be addressed before CNT based transformers could outperform the standard devices. The details of the work are published.^[11]

8. Conclusions

Providing a reliable and highly efficient system for the delivery of electrical energy is one of the key factors that will enable the continued prosperity of our society. Current engineering solutions to this issue have been optimized over a considerable period of time and any radical improvement in the efficiency and cost-effectiveness of energy transfer systems may only be obtained through the use of novel materials and technologies. Carbon nanotubes, have been recognized as extremely promising candidates to fulfill this task, mainly in their application as the next generation of electrical wires.

The production of macroscopic assemblies made purely of nanotubes has facilitated research towards the development of such carbon nanotube (CNT) electrical wires which could replace traditional metal ones. The CNT fibers, which are intended to serve as the conducting cores of CNT wires, are

already produced with virtually no limit to their length and with a wide range of cross-sectional areas. The methods of manufacturing are easy to scale up and are cost-effective. The material obtained is much less dense than any metal, which may be highly advantageous for many applications where the weight of the wiring is crucial. Some of the properties already exceed the performance of conventional conductive materials e.g. the maximum current density possible to obtain in CNT fibers is particularly high. It has been demonstrated that mechanically CNT fibers can outperform any conventional metals used for wiring, when the weight factor is taken into consideration. The fibers are also resistant to harsh chemical treatments, where copper wires can be destroyed within hours or days. Specific conductivity i.e. conductivity divided by density of CNT fibers can be higher than of both copper and aluminium when the fibers are strongly doped. However, to obtain the same conductive properties in the as-made CNT fibers, better control over the morphology of the fibers is required. Therefore, further research in this area is needed. Finally, it has been demonstrated that CNT fibers may be fitted with suitable electrical insulation and easily connected with other parts of an electrical circuit.

The first experiments deploying CNT wires in electrical devices have been successful and proved that CNT wires can replace conventional copper wires in certain applications. Overall, the state of the art results of the research in the field provide good prospects for the application of CNT fibers in electrical wiring.

All the above described research shows that the CNTs may become serious competitors to the existing metallic conductors. Assuming that the rapid progress which has taken place in the field over recent years continues, we may expect that with further basic research we will be able to produce well controlled CNT wires able to outperform traditional metal wires.

The immediate next steps in this area are definitely best placed within industrial research and development, as the technology needs to be scaled up to reach a suitable manufacturing capacity. This will also allow the predicted decrease in manufacturing costs to be achieved. It is, therefore, very promising that the first spin off companies are already in place and have started working towards these goals.

Finally, further development of this field will also depend on both industrial and political involvement. Taking into account that the current wiring systems have been developed and used for more than hundred years, and that they are one of the key elements of infrastructure and manufacturing in a number of countries, the new CNT wires will be a highly disruptive technology. Therefore any move to replace the existing materials will require support from both policymakers and major investors, who will need to have a deep understanding of the requirements of our civilization's energy future.

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