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Low temperature electrical transport in modified carbon nanotube fibres

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Carbon nanotube fibres are a new class of materials highly promising for many electrical/electronic applications. The range of applications could be extended through the modification of their electrical transport properties by inclusions of foreign materials. However, the changes in electrical transport are often difficult to assess. Here, we propose that the analysis of resistance–temperature dependencies of modified fibres supported by a recently developed theoretical model may aid research in this area and accelerate real life applications of the fibres.

Keywords: Carbon nanotube fibres; Modified fibres; Resistance–temperature dependence; Electrical transport modifications

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Carbon nanotube (CNT) fibres, i.e. macroscopic wire-like assemblies of axially aligned CNTs, are highly promising materials for many electrical and electronic applications including wires, electrodes and sensors [1–3]. As CNT fibres are highly porous and made of carbon nanomaterials they may be intentionally or accidentally doped/-combined with other materials [2,4–8]. Such processes introduce changes in their transport properties. It may be highly useful, resulting in new functionalities of the fibres, or harmful, hindering their potential applications.

Often, it is difficult to assess the impact of foreign molecules on the electrical transport of the fibres, and a simple measurement of conductivity at room temperature is not enough for this purpose. Much more useful could be the measurement of resistance–temperature (R–T) dependencies. The R–T characteristics may change gradually from very metallic to semiconducting depending on the morphology of the fibres and foreign inclusions. To provide extreme examples, highly pure fibres made of armchair CNTs or fibres heavily doped with acids may show a decrease in resistance down to 40–50 K, and only below this crossover temperature show a weak semiconductor-like increase in resistance towards 0 K [4,5,9]. On the other hand, poor quality fibres or fibres composited with non-conductive polymers may show an insignificant contribution of metallic type behaviour and, above room temperature, a crossover to a steep semiconducting slope [9–12].

We have recently shown that in-depth analysis of R–T curves may aid an assessment of the influence of the exact morphology of the fibres, determined during the production process, on their electrical transport, and thus the usefulness of the employed process [9]. Here we show that a similar method may be used to provide insight into the changes of transport in CNT fibres due to their modification by foreign molecules.

The CNT fibres tested in all experiments were prepared via a floating catalyst chemical vapour deposition method (described earlier [1,13,14]) using methane and thiophene feedstock. The electrical transport in the fibres was modified by the addition of formic acid, polyethylene glycol grade 200 (PEG), silver nanoparticles (from silver paste – a commercial dispersion of silver in organic solvents) and naturally by the presence of pre-adsorbed water vapour.

The tested fibres were connected on a printed circuit board (PCB) plate with etched copper paths. The sample was connected in a four point probe system. The external and internal paths used for the current and voltage circuit respectively were 40 and 30 mm apart. The fibre was attached via silver paint to copper paths and these were soldered to the further copper wiring. Samples intended for infiltration with polyethylene glycol (PEG) or silver nanoparticles were placed on a holder with raised copper paths so as to decrease the interaction of the fibre with the plate at low temperatures. PEG and silver paste were spread

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along the samples by immersing the fibres in a droplet of the desired liquid produced at the tip of a glass pipette or between tines of tweezers. The droplet was then moved along the fibre several times. For the measurements which required annealing at 770 K in an external furnace, the PCB was replaced with a specially cut out alumina plate, with fixed copper wires replacing the etched copper paths.

The measurements were performed in a cryogen-free cryostat VarioxAC (Oxford Instruments). The sample space was degassed to low vacuum and filled with gaseous helium to accelerate the temperature equilibration between the sample and the cryostat. The temperature of the fibre was measured using a cryogenic sensor (Cernox) mounted close to the sample. The resistance measurements were performed using a DC current of 100 μA to avoid any internal sample heating, and the results were recorded by a computer for further analysis.

To allow quantitative analysis of the changes in R–T curves mentioned in the introduction we have developed a new theoretical model [9]. The main formula Eq. (1) used for fitting the data was derived based on Landauer-type equations and an assumption that the current transfer in the overall fibre is a thermally activated statistical process:

$$R = R_{T_0}\left[\exp\left(-\frac{T_A}{T}\right) + \left[1-\exp\left(-\frac{T_A}{T}\right)\right]\exp\left(-\frac{|T-T_0|}{T_C}\right)\right]^{-1} \qquad (1)$$

Here, T_0 and R_{T0} represent the crossover temperature between semiconducting and metallic types of slope, and the resistance at T_0, respectively. These are experimental values used as input parameters. Due to the fact that R_{T0} may be taken as either an absolute or a relative value without influencing the other fitting parameters, to facilitate comparison between samples in all the following experimental curves the resistance will be presented as a value relative to the resistance measured at 273 K for a given test, and R_{T0} used as a relative value at T_0.

The output parameters obtained from the fitting are activation energy T_A and correlation temperature T_C. T_A describes energy necessary for transfer of charge carriers between nanotubes and is lower for more metallic samples. T_C defines a shape of semiconducting part of the curve and increases when the slope is steeper and wider i.e. for more semiconducting materials. The above model supplemented with an exponential term, for scattering in quasi 1D metals $\beta \times \exp(-\delta/T)$, where β and δ are fitting parameters, allows fitting of R–T curves in the whole range of temperatures and facilitates comparison between samples [9,15,16]. The latter term although it provides values consistent with the previous literature, will not be considered in detail here, as its rigorous derivation still needs further study [9,17].

Fitting of resistance–temperature curves of fibres modified by foreign molecules with the model presented above may provide interesting information on the changes in the electrical transport of the fibres. For this purpose four types of inclusions were tested: water vapour naturally adsorbed into CNT fibres, intentionally introduced acid and silver nanoparticles, all of which cause an increase in conductivity, and for comparison, an insulating polymer that has the opposite effect.

Recent reports show that CNT fibres exposed to ambient conditions naturally adsorb water vapour which improves their conductivity [8]. The exact mechanism is still debatable however it is definitely related to intrinsic electronic changes in the CNTs or their interconnects. This is reflected in the R–T curves, which gradually move towards more semiconducting type upon removal of water molecules. Figure 1(a) presents three R–T curves of a fibre exposed for several months to ambient conditions (35% RH, atmospheric pressure, room temperature) and further annealed in the chamber of the cryocooler using first a DC current of 17 mA for 10 min (1st annealing) and then 19 mA for 10 min (2nd annealing). The sample resistance at 273 K initially amounted to 412 Ω and, after the first and second annealing processes, increased to 818 Ω and

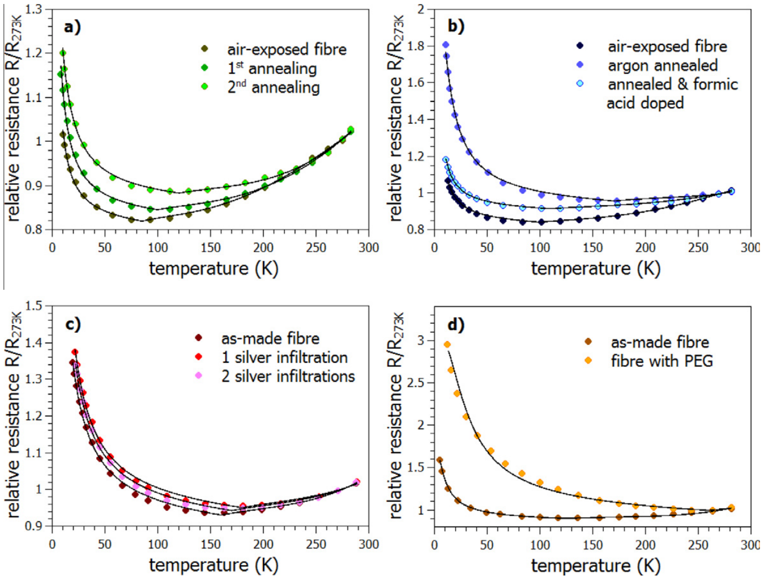

Figure 1. Changes in the resistance–temperature dependencies for (a) current annealing of air-exposed sample, (b) argon annealing and acid doping of air-exposed sample, (c) infiltrations with silver nanoparticles, and (d) PEG of as-made samples. The resistance in each plot is related to the resistance measured at 273 K during the given test. Black lines are fits to the curves with percentage errors, obtained using Scaled Levenberg–Marquardt and Nelder–Mead Simplex algorithms, of less than 10%.