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Resistance-heating of carbon nanotube yarns in different atmospheres

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ABSTRACT

Annealing and functionalization of carbon nanotube yarns (CNYs) is a prospective way of increasing the electrical conductivity of this material. We show a novel way, the simultaneous annealing and instant coating of the CNY by its resistance-heating in atmospheres of hydrocarbons. This method is capable to preserve the lightweight properties of CNYs and increase the electrical conductivity. It could be raised by a factor of 2 through carbon deposition onto the yarns and the carbon nanotubes (CNTs) inside the yarn structure. By resistance-heating over a multistep process the conductivity could be even increased by a factor of 2.2. Comparison of annealing under atmosphere of different hydrocarbons and at different temperatures reveals the influence of resistance-heating on the structure of CNY.

1. Introduction

Individual carbon nanotubes (CNTs) possesses many excellent and partly outstanding physical properties. This includes high thermal [1] and electrical [2] conductivities and high tensile strength [3]. However, for the most mundane applications a CNT bulk material would be needed, so transferring these outstanding properties from nano to bulk scale is a major challenge in the field of CNT research. One of the most promising candidates to fulfill these requirements for different applications are CNT-yarns (CNYs). However, their measured properties, such as mechanical strength or electrical conductivity, are significantly lower compared to individual CNTs [4]. To compensate these drawbacks, a whole range of methods is available which can be divided into four major groups: densification of the yarn [5], coating the yarn [6] or CNTs [7] with metals, functionalization with different substances (halogens [8], acids [9], metals [10] and other molecules [11]) and annealing [12,13]. Normally high temperature annealing is used to improve the structure of individual CNT by healing of structural defects and enhancing the crystallinity [14,15]. This method provides a reagent free way to improve the conductivity of CNYs. The most annealing is done with external heating of the CNY, only a few works reported a direct resistance-heating of carbon nanotube yarns and films to create light emitting devices [16–19]. Coating besides annealing is also a promising way to enhance the electrical conductivity of yarns. Metals are usually used and preferred for coating, but this leads very often to the loss of the advantage of CNY [6] – their lower density [20–24] in comparison to common used metals wires of copper and aluminum. In this case, it is to favor a material, which has the same or lower density as the yarns. One candidate is carbon itself. Until now to our best knowledge, a carbon coating of CNT yarns is not established.

In this work we present a new approach to enhance the electrical conductivity of CNYs. CNT yarns were heated up in different atmospheres by applying a direct current to the yarn itself. As result, the yarns were direct treated by high temperature annealing through resistance-heating. When applying resistance-heating in a carbonaceous atmosphere the yarns were also coated with a carbon layer which significantly increases the conductivity.

2. Experimental

CNYs were spun from a CNT array (Fig. S1a) and mounted on a costume-designed U-shaped sample holder (Fig. S1b). The synthesis of the used CNT array and detailed SEM observations of similar CNYs can be found elsewhere [25]. The parameters for spinning the yarn were 1000 turns per min with a spinning speed of

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40 mm/min 45 mm long samples of CNY where fixed on both sides on Cu-tape. To ensure a good electrical contact between the Cu tape and the CNY, Ag paste was applied and dried at ambient condition overnight. So the effective heat treated sample length reduced to 25 mm because of this contacting method (see Fig. S1). After spinning and connecting the yarns to the sample holder the pristine samples were assembled into a vacuum chamber. Inside this chamber the CNYs were treated through resistance-heating in vacuum (Fig. S2), methane (CH_4) or ethene (C_2H_4) atmosphere, respectively. The chamber could be evacuated to the vacuum in the range of 10^{-5} Pa, nevertheless the experiments at vacuum conditions were conducted at around $1–2 \times 10^{-4}$ Pa. The flow rates for methane and ethene through the chamber were 20 and 40 sccm. Current densities of 50–250 MA/m^2 in the case of vacuum and 100 and 200 MA/m^2 in the case of methane and ethene were applied for 1, 30, 60 and 120 min to the yarns. The direct current (DC) was applied to the yarn by a DC-voltage-current source monitor (ADCMT, Japan). Besides the one step processes of resistance-heating in vacuum, methane and ethene, there were conducted also multistep annealing experiments. In the first step the yarns were resistance-heated in vacuum for 60 min at a current density of 200 MA/m^2. Subsequently the CNY annealed in vacuum were resistance-heated for 30 min at 200 MA/m^2 in an ethene flow of 40 sccm. In the final step the yarns were annealed at 100 and 150 MA/m^2 for 30, 60 and 120 min in vacuum. After every step the CNYs were investigated with SEM and the electrical conductivity was measured. All conducted multistep experiments can be found in supporting information (Table S1).

The CNT yarns were investigated by SEM (JSM 6060LA, Jeol, Japan) and TEM (Tecnai F30, FEI, USA) before and after the annealing process. Measurements of the yarn diameter were realized with the program ImageJ. Characterization with Micro-Raman spectrometer (Horiba Jobin Yvon, France) was realized in the range between 1000 and 1800 cm^{-1} at a wavelength of 514.5 nm (Argon-Laser, Coherent, USA). The I_D/I_G ratio was calculated from the Raman spectra by dividing the intensity of the D-band through the intensity of the G-band. The electrical conductivity of the CNY was measured by two-point measurement with a DC-voltage-current source monitor (Advantest Corp., Japan).

3. Results and discussion

In the following part the measured properties for pristine yarn and resistance-heated yarns under different atmospheres will be presented and discussed beginning with the pristine yarns as a basis of all experiments.

3.1. Pristine yarns

The pristine yarns were examined by SEM, TEM (Fig. 1) and Raman spectroscopy. Measured by SEM, the average diameter of the CNT yarns amounts to 17.6 ± 3.4 μm. Consisted of CNT with 2–4 walls the pristine yarn possesses an average conductivity of 358 S/cm. The number of walls were determined by TEM as well as the average outer diameter of the CNT of 5.7 ± 0.9 nm. The TEM images (Fig. 1c) also reveal that the surface of the nanotubes is partly covered with amorphous carbon. Investigations with Micro-Raman indicate a relatively high value for the I_D/I_G-ratio of 0.82. The TEM and Raman results are in good accordance, although the CNTs consisting of straight graphitic walls the amorphous carbon leads to an elevated I_D/I_G-ratio but in good agreement compared to other double walled CNT materials [26].

3.2. Resistance-heating under vacuum condition

In the following will be presented the properties of the yarns after their heat treatment in vacuum. The yarns began to glow being resistance-heated under vacuum. The glowing color is changing from red at an applied current density of 50 MA/m^2 to bright shining at 250 MA/m^2, which indicates a rising of temperature with increasing current density. A measuring of the temperature of the yarn was not possible, nevertheless in comparison with literature [16] the estimation gives the temperature in the range of 1500 and > 2000 K if the color of incandescence is matched [see Fig. S2]. The SEM images (Fig. 1b) of yarns heated under vacuum show a transformation of the surface of CNY. The high temperature treatment eliminate all entangled CNTs. Also a slight decrease of the average diameter of CNY is observable. This shrinkage of the CNY could be caused by electromechanical contraction during the resistance-heating [27]. Both effects lead to a dense looking yarn and a smoother yarn surface. Detailed view of the CNTs using TEM analysis demonstrates a big difference in their appearance before and after the heat treatment in vacuum (Fig. 1 c, d). Hardly any amorphous carbon is observable at the surface of the CNTs after the resistance-heating under vacuum conditions. This leads to the conclusion that the disordered carbon covering the external walls of CNT evaporates during heat treatment under vacuum. Besides the evaporation of carbon the CNT shell structure gets more irregular.

The high temperature treatment of CNYs in vacuum leads to a slight increase of their electrical conductivity. Yarns which were heated for 2 h showed the strongest effect, so in the study only these results will be discussed in detail. An overview of all realized heating experiments in vacuum is presented in the supporting information (Fig. S3). The measured conductivities were 349, 423, 336 and 424 S/cm for the yarns which were treated for 2 h with current densities of 50, 100, 200 and 250 MA/m^2 respectively. Even though the conductivity of the CNYs is not changing significantly, the I_D/I_G ratio calculated from the Raman spectra shows a strong response to the resistance-heating. Here the values range from 0.77 ± 0.03 to 0.26 ± 0.02 and 0.05 ± 0.003 for 100, 200 and 250 MA/m^2 (annealed for 2 h), respectively.

If we compare the measured electrical conductivity with the TEM results (Fig. 2b) and Raman data and keeping the both facts in mind: i) evaporating of amorphous carbon from the CNT surface and ii) high temperature causing an irregular CNT structure, it is not surprising that no big change in conductivity of the yarns could be observed. In the case of resistance-heating under vacuum conditions contrary effects compete with each other. With rising temperature amorphous carbon evaporates and causes a decreasing of the I_D/I_G ratio while the increased defect density decreases conductivity at the same time. Compared to Niven et al. [12] where yarns were also annealed at high temperatures, one can see converse results for the behavior of electrical conductivity. A possible explanation comes from the different conditions during annealing. Niven's heating experiments are executed with external heating under Argon atmosphere. This is fairly different to the here used approach of direct heating under vacuum conditions. Nevertheless our results are fitting to simulations where the effect of irradiation to carbon nanotubes is described [28]. Irradiation causes a continuous extraction of carbon atoms from lattice, through atomic rearrangement the shells are reconstructed into an irregular structure. So it could be expected that the high temperature annealing in vacuum by resistance-heating removes not only amorphous carbon but also leads to atomic rearrangement of carbon atoms in the shells of CNT and to an appearance of an irregular shell structure which is still graphitic.