Temperature response of carbon nanotube networks

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Abstract. Carbon nanotube networks were assembled by dielectrophoresis on microelectrodes and their response to temperature was monitored. The stability of the networks was investigated in order to determine their suitability for use as electrical components or sensors. Our results suggest that the networks cannot readily be used for these applications since their behaviour depends greatly on the amount of oxygen adsorbed on their surfaces.

1. Introduction
Since their discovery in 1991 [1] carbon nanotubes have been studied extensively in terms of their mechanical and electrical properties and have become components in novel devices ranging from probe tips for scanning force microscopes [2] to field effect transistors [3,4] and conductivity-based gas sensors [5,6]. Nanotubes may be integrated onto electrodes using several methods, such as AFM manipulation [7], surface patterning [8] and direct growth [9]. Recently, several groups have taken up dielectrophoresis (DEP) as a method for assembling nanotubes on circuitry [10]. The nanotubes are dispersed in a solution, typically an organic solvent or a surfactant, in which they are exposed to a strong, inhomogeneous electric field via an immersed set of electrodes.

In this work we study the response of single-walled carbon nanotubes (SWNTs) to moderate variations in temperature and humidity. The SWNTS are assembled as ordered networks on microelectrodes using DEP [11]. Such easily assembled networks are of interest for applications previously demonstrated with individual SWNTs, such as field effect transistors and sensors.

Though a number of studies document the behaviour of nanotubes under extreme heating or cooling, only few address the response of carbon nanotube networks (CNN) to heating in a temperature range of practical importance for electronics applications. In this paper we will show how the resistance of CNN behaves when heated from room temperature (RT) to temperatures up to 100°C. We will show that heating the CNN triggers a complex response that can satisfactorily be explained by oxygen desorption and that the sensitivity of the CNN increases with increasing initial resistance.

2. Materials and Methods
A small quantity (ca. 0.3 mg) of SWNTs from Tubes@Rice was added to a 1 % water solution of Sodium Dodecyl Sulfate and ultrasonicated for 15 minutes with a 150 W ultrasonic disintegrator and then for 4 hours in a 30 W ultrasonic bath. After a few months the upper part of the solution, likely to contain individual SWNTs or bundles too light to be affected by sedimentation, was used for the experiments. The nanotubes were assembled simultaneously on two pairs of identical microelectrodes.
by applying an AC voltage of 10 V peak-to-peak at a frequency of 10 MHz for 40 seconds. After the voltage was turned off a stream of nitrogen gas was used to dry the sample [11].

The CNN were placed in a custom-made chamber (Figure 1b) capable of being pumped down to under 0.1 Pa and heated to a maximum of 150°C by a heating ribbon wrapped around it. Sensors inside the chamber monitor the pressure and the temperature. The latter was controlled by adjusting the voltage output to the heating ribbon via a feedback loop, enabling also the control of the heating rate. A Labview program recorded the pressure, temperature and up to four multimeter (Keithley 2000) readings in real-time. Nitrogen gas could be applied into the chamber through a dedicated valve. Water could be injected into the chamber under vacuum through a membrane.

Figure 1. (a) The microchip used for the assembly of nanotube networks. The electrodes are made of 100 Å Ti and 1000 Å Au on a 500 nm thick silicon oxide. The gaps are 1 µm. (b) Drawing of the chamber used for the experiments.

The experimental procedure used to investigate oxygen desorption during heating was as follows: (i) The networks were heated to 50°C and kept there for about 10 minutes. (ii) The chamber was evacuated to about 80 Pa and subsequently filled with nitrogen. (iii) The CNN were heated further to 70°C and kept there for 10 minutes; the heating was turned off and the CNN were left to cool down for about 1 hour. (iv) When the temperature had reached about 30°C the chamber was evacuated again to about 80 Pa and then refilled with nitrogen. (v) The CNN were then heated again to 70°C, kept there for about 15 minutes and then cooled down to 50°C.

Injection of various quantities (from 10 µl to 450 µl) of water in the chamber under vacuum at RT and in the temperature range 50 – 60°C was also done to further clarify the recorded behaviour.

Experiments were carried out on twelve samples, which all showed the same behaviour described in the results section. The resistances of the networks were in the range of 1 – 10 kΩ, which makes direct comparison of the response curves difficult. Therefore, in the following sections, the resistance of the networks is presented as normalized to the initial value.

3. Results

As shown in Figure 2a, the resistance decreases roughly linearly as the temperature is increased to 80°C, and then starts to increase. This point, referred to as the turnover point (TP) from now on, varied between 40 and 100°C in the studied samples (see Figure 2b). The solid black line in Figure 2b shows were the points should have been if the networks could readily be used as temperature sensors.

Oxygen is known to play an important role for the conductance of carbon nanotubes [6]. Heating the CNN should cause adsorbed oxygen to leave the nanotube surface, thus increasing the resistance of the nanotubes. We suggest that this accounts for the change in behaviour of the resistance during heating. To investigate this, a series of measurements was carried out, as described in section 2. By evacuating the chamber to about 80 Pa in steps (ii) and (iv) any oxygen released from the network during heating is removed. The chamber is refilled with nitrogen gas to facilitate heat exchange. The addition of nitrogen gas in the chamber does not in itself cause a change in the CNN resistance.
Figure 2. (a) The resistance of two different CNN normalized at the heating starting point. The heating is carried out at atmospheric pressure in air. (b) The turnover point for different networks as a function of the maximum heating temperature.

Figure 3. (a) The normalized resistance of two samples is shown, while heating to various temperatures and while twice evacuating the chamber of air and filling it with nitrogen. (b) The temperature response of the same networks before (i) and after (v) oxygen evacuation is presented.

Figure 3 shows the normalized resistance of two CNN during this series. Steps (i) to (iv) are plotted in Figure 3a, while steps (i) and (v) are compared in Figure 3b. The chamber was evacuated at a point where the resistance of the networks was still increasing, despite the drop in temperature, because, if indeed oxygen desorption is taking place, then the desorbed oxygen will be evacuated from the chamber as well. On the time axis $t = 0$ corresponds to the start of the heating process and the time lapse between the last point in Figure 3a and the point at $t = 0$ in Figure 3b is about 10 minutes.

As Figure 3b shows, there is indeed a difference in the response between steps (i) and (v). After the chamber evacuation, when the oxygen content of the chamber is about 0.00002%, the resistance of the CNN decreases almost linearly during heating. Only after keeping the CNN at the high temperature for about 10 minutes the resistance starts to increase. In contrast, when the experiment is in air in step (i), the TP occurs at 44°C despite the ongoing heating.
Since the evacuation of the chamber also removes any water present in the atmospheric air, we also investigated the effect of water on the CNN resistance. As seen in Figure 4, injecting various quantities of water in the chamber leads to a resistance increase immediately upon injection.

![Figure 4](image)

**Figure 4.** The normalized resistance of the networks when they are exposed to various quantities of milli-Q water in vacuum at room temperature. The inset shows similar measurements at a higher temperature. In the graphs $t = 0$ corresponds to the point in time where water is injected.

### 4. Discussion

We have presented a series of measurements designed to clarify the rather unusual behaviour of CNN during heating. The results lead to the conclusion that this behaviour, as shown in Figure 2a, is due to the desorption of oxygen molecules from the surface of the nanotubes.

Before the TP is reached, the network resistance changes almost linearly with temperature, with a negative slope – the sensitivity of the network. After each heating step, subsequent chamber evacuation and refill with nitrogen, the TP is delayed (Figure 3b), but the sensitivity remains the same. The sensitivity clearly depends on the network itself, being greater for the networks with the larger initial resistance (Figure 5). The maximum sensitivity measured was $0.5\%/°C$, a rather small value indicating a dominance of metallic nanotubes in the conductance. This may be related to the network being dense, which leads to an average metallic behaviour [12], or to the high AC frequency of 10 MHz used for the assembly process, which should favour the trapping of metallic nanotubes [13].

![Figure 5](image)

**Figure 5.** The percent change in the resistance per degree Celcius for a number of carbon nanotube networks as a function of their initial resistance. The larger the resistance of the networks, the better the sensitivity.

The studied CNN can be considered as bundles of SWNTs stacked into several layers between the electrodes. When the CNN are heated, oxygen adsorbed on the outer surfaces of the networks will desorb with a temperature dependent rate, while oxygen from the inner surfaces must first diffuse to the surface of the network before it can escape, which is slower and requires more energy. This could explain the recorded behaviour: During the first heating step, most of the oxygen on the outer surfaces of the network desorbs at a high rate, which leads to the early increase of the resistance. At the second heating step the resistance again starts to decrease, whereas the TP occurs at a higher temperature due to the slower diffusion of oxygen trapped in the network. Repeating the procedure is expected to eventually clean the sample of oxygen, resulting in a linear temperature dependence of the resistance.

Even though all networks have been assembled using the same experimental procedure and parameters, there is a certain spread in their resistance values related to the stochastic nature of the
assembly process [11], which gives rise to fluctuations in number of nanotubes, contact properties, configuration and perhaps even distribution of metallic and semiconducting nanotubes. More nanotubes and/or fewer semiconducting nanotubes would lead to a smaller network resistance and a denser network. It was shown in [12] that random dense networks behave mostly like metals, while less dense networks behave like semiconductors. We observed that the sensitivity of the CNN to temperature variations was smaller for networks with the smaller initial resistance, i.e. those likely to be denser and therefore according to [12] showing a metallic behaviour.

The humidity response of unordered CNN has previously been discussed in the literature [14-16] with varying results. In [14] and [15] the authors note that while the resistance of the nanotubes increases at first, further increase of the humidity [15] or the water vapour injection volume above a certain value leads to a subsequent decrease [14]. In [16] the authors note an increase in the resistance at 80% relative humidity. The latter result agrees with this paper, with the difference that the resistance here does not recover when the water is removed by evacuating the chamber. However, the increase in the resistance does depend on the injected volume as well as the history of water injection.

In summary, we demonstrated that CNN assembled by DEP show a complex behaviour when heated. Therefore, such networks would not be readily suitable as electronic components, where temperature modulations up to even 30°C above RT are not uncommon. However, when cleaned and isolated from oxygen, the response of such networks to temperature can be modelled and taken into account for electronic designs. Furthermore, the cleaned and oxygen-free packed networks have the potential to be used as temperature sensors, where a small size, a simple temperature-resistance relationship and a larger range is required. The sensitivity of the networks to temperature depends on their initial resistance, which in turn is a measure of the density of assembled nanotubes, the fraction of semiconducting nanotubes in the network and the contact resistance. Since the response to water vapour is both irreversible but also dependent on the device history, it is unlikely that these networks are suitable as humidity sensors, but more investigation is needed to clarify this point.

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