

Oxidation of CVD Grown Carbon Nanotubes for Applying Magnetic Complexes for Spin Transport Measurements

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Abstract and Introduction:

Due to their high aspect ratio and few nuclear spins, carbon nanotubes (CNTs) can be used as one-dimensional models to observe fundamental spin transport. Polarizing electron spins have been done on CNTs by attaching individual magnetic complexes. Different magnetic complexes and attachment mechanisms have been used [1], but the one of interest here are tetramanganese (II) complexes with manganese as the metal [2, 3]. Regardless of the complex however, functional groups need to be introduced to the CNTs in order to chemically attach the complexes.

For this aim, the CNT networks were oxidized at 420°C in air, pure O₂, and an ~ 50/50 mix of N₂/O₂ to control the oxidation rate. To measure the degree of oxidation, Raman spectroscopy and resistance measurements across CNT networks were done. An increase in oxidation was expected to show a decrease in resistance and an increase in defects in the CNT network. At 420°C, the results showed that there were no significant effects on the tubes. Although at 450°C, results from previous experiments showed an increase in defects from the Raman spectroscopy [4].

Methods:

CNTs were grown in a tube furnace at 860°C on a one-cm² quartz substrate using a Fe/Mo catalyst. Using this procedure, networks of CNTs were grown on the substrate and then Ti/Pt (3/70 nm) contacts were deposited on the pristine networks. Figure 1 shows how these square contacts were distributed on the quartz substrate along with an atomic force microscope (AFM) image of the networks. The tubes were oxidized in air, pure O₂, and an O₂/N₂ mixture. In air, the tubes were oxidized in a muffle oven. Pure O₂ and O₂/N₂ oxidations were performed in a tube furnace. The gasses bubbled through water before going into the oven because COOH groups are needed for a latter functionalization [2].

The CNTs were characterized by a Bruker RAMII spectrometer with Fourier-transformed Raman measurements at an excitation wavelength of 1064 nm. Figure 2 displays an example of a Raman spectrum data with the D and G peak labeled. The ratio of the area underneath the D and G

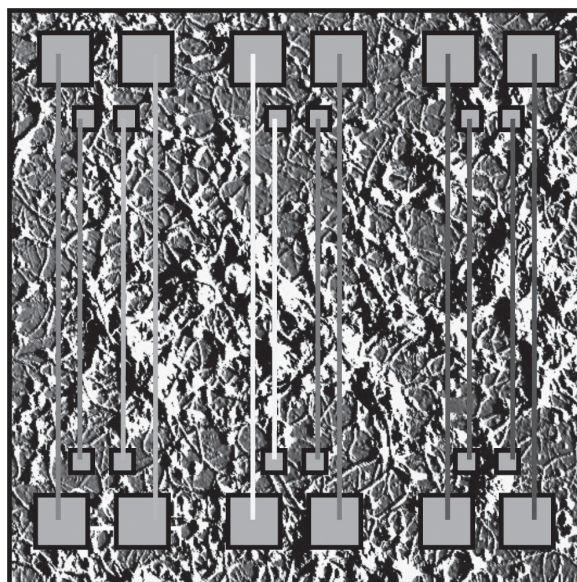


Figure 1: The contacts were arranged on the substrate with the contacts represented by the grey squares. A “large vertical” configuration is shown with the large lines being current and the short lines are voltage measurement. The sets of colors show that we can perform six measurements across the sample. The 10-micron by 10-micron AFM image underneath shows the networks on the substrate (not to scale compared to the substrate).

peak was sensitive to the number of defects created and was obtained by using a numerical approach. The peaks were subtracted from a linear background and then a trapezoidal rule was performed to get the areas and ratios.

The resistance across the CNT network was also measured using two probe and four probe measurements. Using the contacts, a current was swept through the network and the voltage drop was measured at each oxidation step to obtain the resistance. Since the samples were not homogenous, different combination of contacts were tried across the sample. Figure 1 represents how a four probe measurement “large vertical” configuration was done.

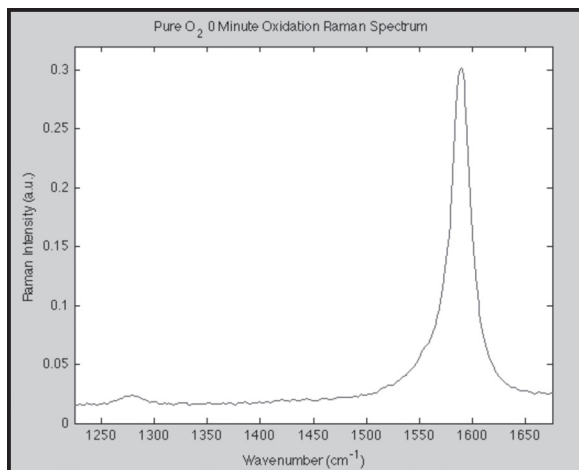


Figure 2: Pure O₂ zero minute Raman spectrum to show the D and G peak shown as the left and right peak, respectively.

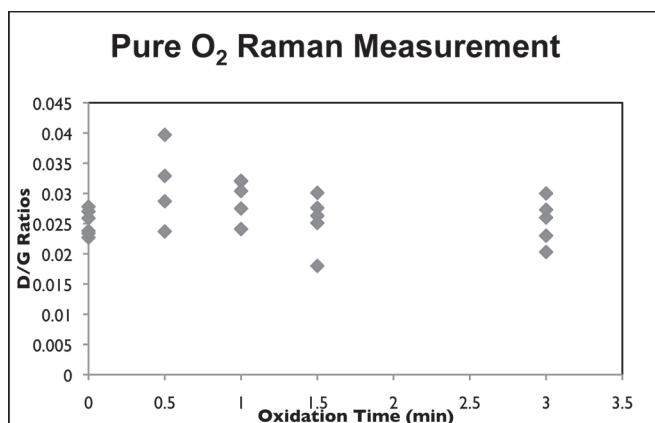


Figure 3: D/G Ratios from pure O₂ measurements. As shown the ratios stay constant within the error of the measurements.

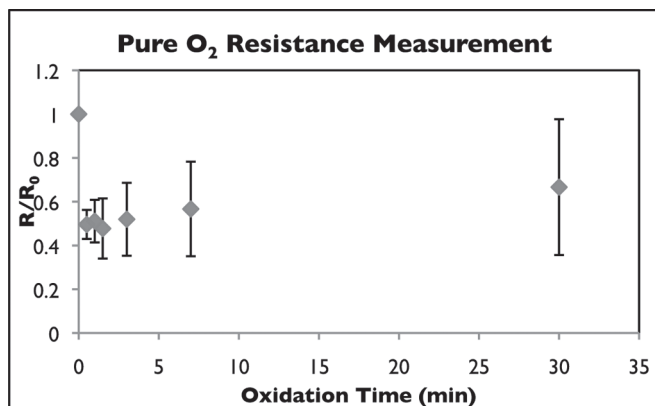


Figure 4: Resistance measurement of the pure O₂ sample from the large vertical configuration shown in Figure 1.

Results and Discussion:

The ratio between the area under the D peak and the area under the G peak stayed constant throughout the oxidation, as shown by Figure 3. The resistance across the channels for all three conditions went down sharply after an initial oxidation of thirty seconds to a minute and then stayed constant within the errors of the measurements until oxidation was stopped after 30 minutes. Figure 4 displays the results of the resistance measurements of pure O₂ with the “large vertical” configuration.

The D/G plots didn’t seem to show strong evidence for defect formation on the CNTs. This was likely due to the fact that 420°C was not hot enough for significant amount of defect formation. With the resistance, the initial drastic drop can be attributed to the CNTs crosslinking, which would create stronger paths for the current to flow through. Afterwards, the resistance stays constant within the errors of the measurements. This agrees with the little to no defects formed on the CNTs. At 450°C, on the contrary, oxidation definitely takes place; the D/G ratio saturates to twice of its original value and resistance decreases until 12 min [4].

Conclusions:

CNTs were grown in a tube furnace in a network on top of a quartz substrate. The CNTs were oxidized in three different manners, pure O₂, N₂/O₂ mix, and air, all at 420°C. These tubes were analyzed using Raman spectroscopy and resistance measurements. The Raman measurements did not show any change in the D/G ratio, but the resistance decreased. The constant D/G ratio was most likely due to the fact that 420°C was not hot enough to create defects on the tubes. The sharp drop in resistance after initial oxidation can be explained by CNTs crosslinking.

References:

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