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Spatial and contamination dependent electrical properties of carbon nanotubes

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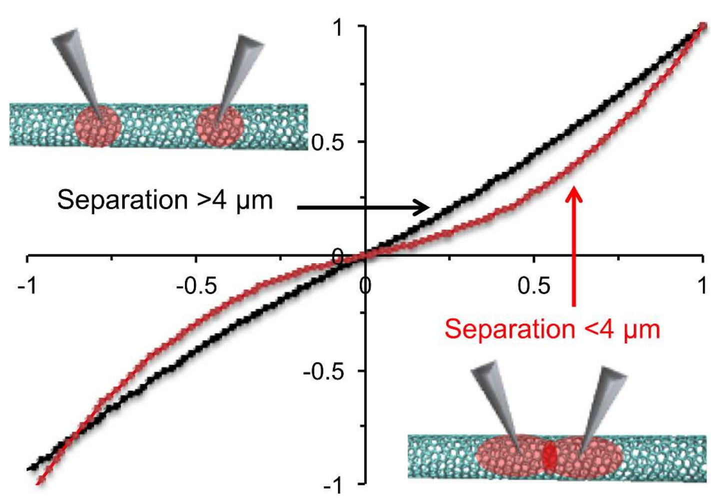
ABSTRACT: Two-point probe and Raman spectroscopy have been used to investigate the effects of vacuum annealing and argon bombardment, on the conduction characteristics of MWCNTs. Surface contamination has a large effect on the two-point probe



conductivity measurements resulting in inconsistent and non-reproducible contacts as well as enhancing the electric field under the contacts resulting from overlapping depletion regions when probe separations are small (< 4 μm) causing very high resistances. Annealing at 200 °C and 500

°C reduced the surface contamination on the MWCNT, but high resistance contacts still did not allow intrinsic conductivity measurements of the MWCNT. The high resistance measured due to the overlapping depletion regions was not observed after annealing to 500 °C. Argon bombardment reduced the surface contamination more than vacuum annealing at 500 °C but caused a slight increase in the defects concentration, enabling the resistivity of the MWCNT to be calculated, which is found to be dependent on the CNT diameter. The observations have significant implications for future CNT-based devices.

KEYWORDS: carbon nanotube, electrical conductivity, argon bombardment, Raman, depletion region

Since their discovery by Iijima,[1] carbon nanotubes (CNTs) have received a considerable amount of scientific interest.[2] Carbon nanotubes have high tensile strength and chemical stability, are a good heat conductor, have low resistivity and depending on chirality can be either metallic (conducting) or semiconducting.[3] These properties have led to CNTs being used in light-weight, high strength composites[4] and electronic devices such as single nanoscale-channel transistors.[5] There have been many studies investigating the conductivity of carbon nanotubes; however, there has been large variations in the results presented for both the CNTs themselves, but also fibers created therefrom.[6] There are a number of reasons for this including whether the tube is single or multi-walled, synthesis type and measurement technique. Another possibility is the effects of surface contamination, which is born out by reports that specific treatments can enhance the conductivity.[7] As we will show surface contamination not only creates barriers for electron transport into the nanotubes but under certain conditions enhance electro static effects resulting in modified transport through the tube itself, which has potential negative implications on future CNT-based device performance.

Our previous work has shown that surface contamination, such as amorphous carbon, hydroxyl groups and adsorbed water, on ZnO nanorods and nanosheets can cause inconsistent and non-reproducible contacts that affect the accuracy of conductivity measurements.[8, 9] There are a number of methods that are commonly used to remove surface contamination from nanostructures including surface passivation, annealing and argon bombardment.[10-12] Work carried out by Lee et al. has shown that rapid annealing to about 800 °C can reduce the contact resistance when measured using Ti/Au deposited electrodes;[13] however, it is not clear whether this is caused by the removal of surface contamination or by an improved contact from chemical changes at the interface as a result of annealing.

As the first stage on a detailed study of the electronic properties of individual and bundles of CNTs we have investigated the necessary treatments to ensure a consistent baseline for conductivity measurements, as well as the relationship of conductivity with tube diameter.

Multi walled carbon nanotubes (MWCNTs) were synthesized using a table top horizontal tube reactor using a previously reported method,[14] and were subjected to microwave irradiation followed by chlorine treatment to remove the majority of residual iron catalyst.[15] The MWCNTs were suspend in ethanol, sonicated, and drop cast on to the native oxide of a Si wafer. The substrate has a resistivity of $>10^3$ higher than the MWCNT measured. For the 2-point probe measurements a sample was mechanically fixed to a sample plate and loaded into an Omicron Lt Nanoprobe (base pressure 1×10^{-11} mbar). Tungsten STM probes were etched in 2 M KOH solution using the method described by Ibe[16] and annealed under vacuum to minimize the effects of the shank oxide on the electrical measurements.[17, 18] The tips were manually approached onto the CNTs using the method described by Smith et al.[19] to prevent strain on the CNTs that could affect the resistance measurements. Current-voltage (I-V) measurements were taken in transmission line fashion along randomly selected individual CNTs with a range of diameters.

The MWCNT investigated were of diameters varying from *c.a.* 40 nm up to *c.a.* 200 nm and with length of *c.a.* 30 μm, as measured from the SEM images.[14] It was also observed that some of the MWCNT were terminated with iron/iron oxide particles that were not removed during chlorination. To insure that the catalyst did not affect the electrical measurements, the tungsten probes where landed away from the metal particle. For each MWCNT the probes where stepped in from a large probe separation to a small separation (e.g., Figure 1) to prevent surface modification due to annealing affecting subsequent measurements. Nevertheless, measurements were subsequently taken with increasing probe separation and it was seen to have no measurable effect on the results. Thus, measurements were taken at a particular probe separation twice in a stepwise manner, starting with a wide probe separation to a small separation and back. In addition, each measurement was made at a particular distance 5 times in order to provide statistical analysis.

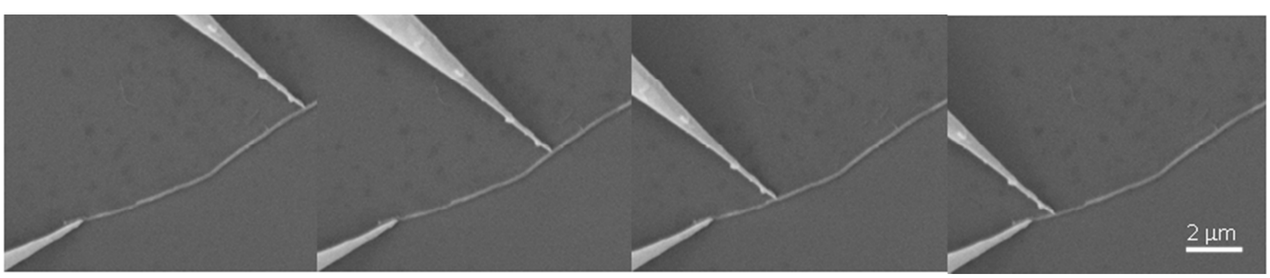


Figure 1. SEM images of a typical measurement on a single MWCNT with the tungsten probe positions in sequence.

For the two-point probe measurements the voltage was swept from -1 V to +1 V; for each probe separation the voltage was swept 5 times to ensure reproducible values. Figure 2 shows a representative plot of resistance against probe separation for each treatment. The resistance was calculated at 1 V and -1 V using the average measured current from the 5 sweeps at each separation; an example of the results in shown in Figure 3a. The uncertainty was calculated using the standard deviation in the 5 repeat current measurements at 1 V and -1 V and propagated with the quotient rule using the standard resistance is voltage over current equation. The resistances calculated from the I-V curves from the untreated sample showed deviation at +1 V compared to -1 V and the error calculated was also typically around 10% that of the resistance. This suggests that the contact between in the tungsten STM probes and the MWCNT is inconsistent.

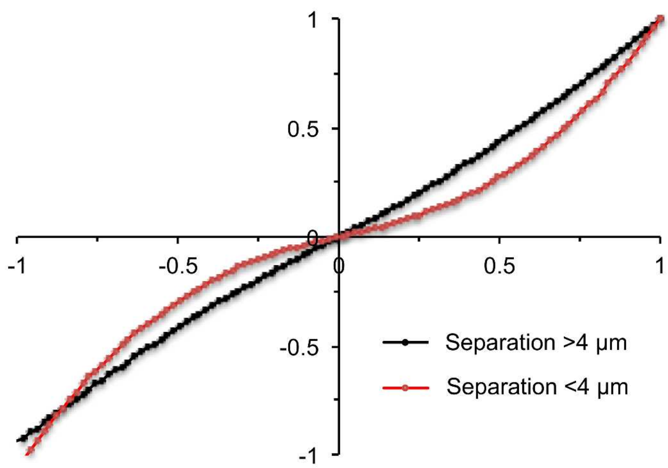


Figure 2. Representative normalized I-V plots of an individual MWCNT measured with probe separations of greater and less than 4 μm.

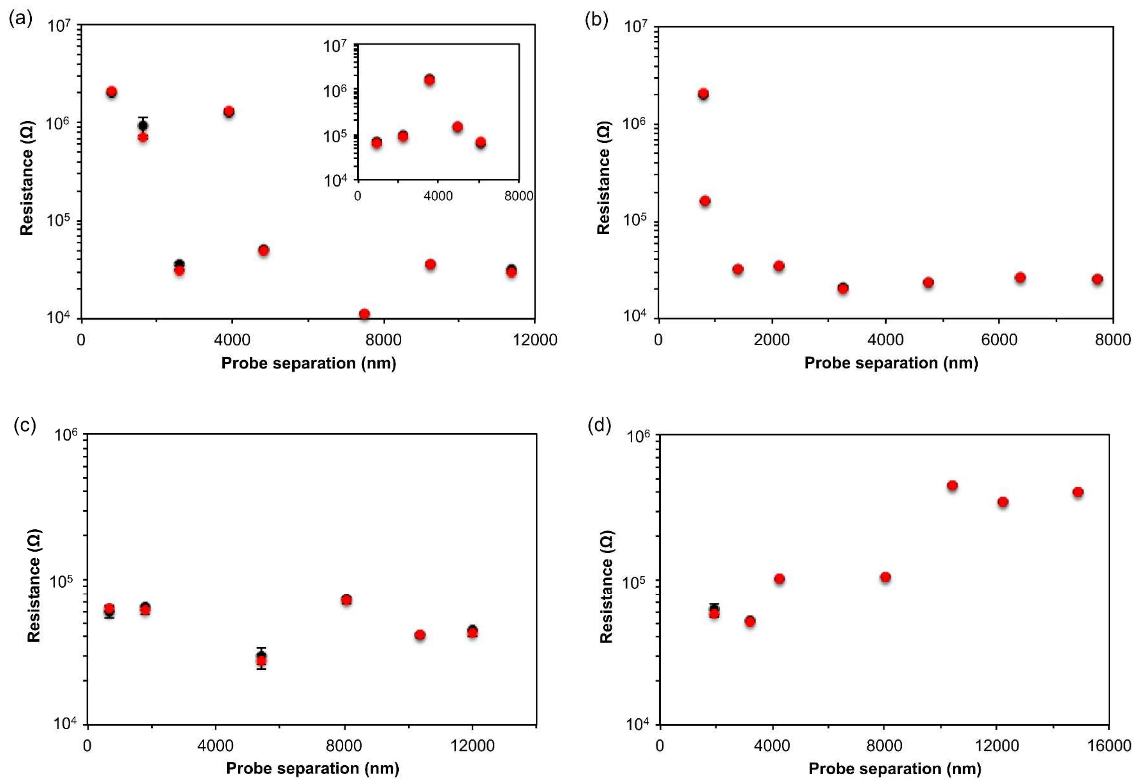


Figure 3. Plots of resistance, as measured at -1 V (black) and +1 V (red), against probe separation for (a) before, (b) after annealing at 200 °C, (c) after annealing at 500 °C, and (d) after argon bombardment. Error bars show the error propagation using the standard deviation in the current for 5 repeat measurements and precision of the voltage.

For a conductor it is expected that resistance would increase with probe separation; however, this was not observed (see Figure 3a). Additional plots are shown in Figures S1-S4 (ESI). For probe separations greater than 4 μm the resistance is scattered. This could be a result of strain caused by the probes on the MWCNT, however, the method used to approach the probes in known to minimize strain on the sample.[19] Instead we attribute this scatter to surface contamination that caused non-reproducible contacts when the probe separation is greater than 4 μm.

We proposed that purification or annealing the MWCNTs should improve this as previous working vacuum annealed ZnO nanosheets showed that annealing to 300 °C and 500 °C improved the reproducibility of the contacts by removing surface contamination.[8] However, this work also showed that the structure and defect chemistry of the nanosheets changed under vacuum annealing, which alter the conduction mechanism.

In general for probe separation of less than, and up to, 4 μm, the resistance decreases with probe separation. This is highly unusual as standard resistivity models state that resistance increase linearly with channel length. We attribute this to overlapping depletion regions induced by the tips creating high resistance contacts.[20,21] It was observed that the I-V curves at separation less than 4 μm were more rectifying in nature than at greater distances (Figure 2). To quantity this straight lines were fitted to the I-V curves (normalized to maximum current) and a R^2 value was calculated. For I-V curve where the probe separation was greater than 4 μm the average R^2 value was calculated to be 0.994, which decreases to an average value of 0.944 for probe separations of less than 4 μm. For some MWCNTs it was seen that for small separations the resistance was lower and increased to a peak at 4 μm before following the decreasing trend (see Figure 3a insert). We believe this is caused by local annealing induced by the high resistance under the tips resulting in better contact, because the current measure for the first sweep is lower than the succeeding sweeps.

To try to remove the surface contamination the samples were annealed in vacuum at 200 °C for one hour, allowed to cool and the I-V measurements repeated (again on at least 6 MWCNTs). The resistance calculated from the sample vacuum annealed to 200 °C were more consistant when compared to the resistance at 1 V and -1 V and the error calculated was also lower than that of the untreated sample with a typical value of 5% that of the resistance. However, there was no clear trend of increasing resistance with increased probe separation suggesting that surface contamination is causing inconsistent contacts and the contact resistance is dominating the measurements. The peak of highest resistance has also decreased to *ca.* 2 μm when compared to the untreated sample, suggesting that the depletion region size has reduced.

To investigate if the surface contamination had been reduced Raman spectroscopy was used to measure any changes in the bonding of the carbon nanotube, both before and after annealing at 200 °C. For each sample Raman spectra were collected using a 532 nm laser from a Renshaw spectroscope, from three areas of the sample with 10 s integration time, with a laser power of 1.7 mW, accumulated 3 time across a spectral range 1000 cm^{-1} to 3000 cm^{-1}. Figure 4a shows the Raman spectra that has been normalized to the G peak and averaged. The G mode originates from sp^3 C-C vibrations and the peak for the untreated MWCNTs is centered at 1582.9 cm^{-1}. The Raman spectra also consists of a D peak centered at 1350.6 cm^{-1} and a G' peak centered at 2700.2 cm^{-1}. The D mode is caused by structural defects hence the ratio of the G to D (G/D) peak is commonly used to indicate the number of defects in the carbon nanotube structure. Vacuum annealing to 200 °C did not significantly alter the G/D ratio from that of the untreated sample and remained at 0.47. The G' mode is the second overtone of the D mode however the G' mode has a high intensity as it involves a self-annihilating pair of phonons and so does not require defects. Vacuum annealing reduced the relative intensity of the G' peak to 0.81 compared to the untreated sample, 0.90. The G' for MWCNT has not been well defined with a physical meaning; however, it is associated with carbon species.[22] Therefore we attribute the decrease in the relative intensity of G' peak to the removal of surface carbon species and a reduction in surface contamination.

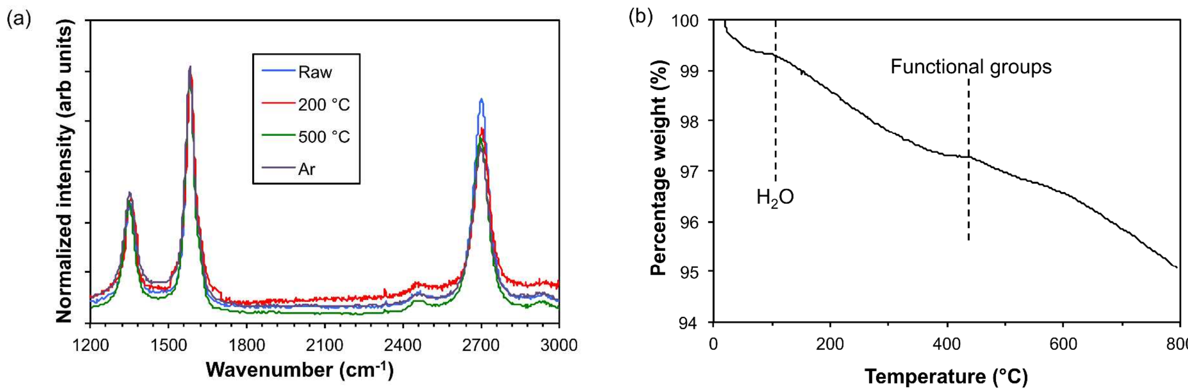


Figure 4. (a) Raman spectra for MWCNTs, after vacuum annealing at 200 °C for 1 hour, after vacuum annealing at 500 °C for 1 hour, and after argon bombarded at 0.3 kV for 5 mins. Spectra have been normalized to the G peak. (b) TGA of MWCNTs showing loss of adsorbed water and functional groups.

To see if these effects where caused by the removal on surface contamination, thermogravimetric analysis (TGA) was carried out on a sample of the MWCNT using a TA Instruments SDT Q600 thermo-gravimetric analyzer, under 100 L/min argon flow with a ramp rate of 5 °C /min up to 800 °C (Figure 4b). After reaching *c.a.*100 °C there is a visible step which is associated with the evaporation of water. There is another step at *c.a.* 450 °C which is attributed to the loss of functional groups such as carboxylic acid and epoxide groups and surface contamination.[23]

Given the additional mass loss at higher temperatures, the MWCNTs were annealed to 500 °C for one hour and I-V measurements taken. The Raman spectra showed no significant change in G/D ratio (Figure 4); however the relative intensity of the G' peak reduced further to 0.73 indicating a further reduction in carbon species.[22] To understand if the further removal of surface contamination caused by annealing at 500 °C has improved the contacts, two-point probe were carried out. The results show a further reduction in the uncertainties calculated with a typical value of 1% that of the resistance. Also the high resistance peak was not observed although this is no trend between the resistance and length (Figure 3c). There was also still some variation between the resistances calculated as 1 V and -1 V. Therefore we can assume that the surface contamination is still causing the contact resistance to dominate the resistance measurements.

Argon ion bombardment is known to be an effective method from removing surface contamination but can damage the surface and incorporate argon in to nanostructures.[24] Therefore, a second sample was loaded into the Omicron LT Nanoprobe and treated with argon bombardment at 0.3 kV for 5 mins. I-V measurements were then made to randomly selected CNTs.

Argon bombardment at 0.3 kV for 5 mins resulted in resistance measurements that were lower than those measured on the vacuum annealed samples (Figure 3d). Typically the resistance calculated at +1 V and -1 V for probe separations less than 5 μm were of the order of 10 kΩ compare to 100 kΩ for the annealed samples. It was also observed that there is no deviation between the resistance calculated at +1 V and -1 V indicating that the contact between the probes and MWCNT is consistent. Error in the resistance was also typically 1%, suggesting that the surface contamination has been removed. The error in the resistance was also typically 1% the value of the resistance. It can also be seen from Figure 3d that resistance increases with length, which is expected for a typical conductor. For small separations (see ESI) there is still some scatter in the resistance versus length plot. This suggests the contact resistance is of the order of the resistance of the MWCNT. Fitting a straight line to Figure 3d and calculating the gradient gives a resistivity value of 2.8 kΩ μm^{-1} which is in agreement with the theoretical values in the literature.[13, 25-27] It can also be seen that there is no increased resistance at small probe separations of the argon bombarded MWCNTs. This suggests that surface contamination can increase the amount of band bending at the contact, most likely due to focusing the electric field at the end of the tip resulting in the high resistance observed. This effect has been seen when the tip has been contaminated with oxygen and carbon.[18, 28]

To see if the reduction in surface contamination could be measured, Raman spectroscopy was carried out. The Raman spectra collected from the argon bombarded sample shows a decrease in the G/D peak ratio indicating an increase in the number of defects (Figure 4). This suggests that argon bombardment, even at a low power causes damage to the nanotube and induces defects. Clearly this is not the issue with respect to CNT-probe interactions, which must be adsorbed species. There was also a decrease in G' peak relative intensity which reduced to 0.70.

Figure 5 shows the resistivity of the MWCNT after argon bombardment against the diameter of the CNTs. The resistivity was calculated by fitting straight lines to the resistance against probe separation plots. It should be noted that, as previously stated for probe separations of less the 5 μm the contact resistance is similar to the resistance of the tubes causing a scattered plot. As such the resistivity calculated will not be accurate and is shown here only to depict a general trend that resistivity decreases with increased tube diameter. However, it cannot be said from our data whether the trend is linear or exponential. However, it would be reasonable to assume the resistivity would not keep decreasing in a linear fashion with increasing diameter. We attribute this trend to an increased number of channels for the current to flow, as the number of the "walls" increases with tube diameter. It should be noted that Figure 5 does not follow the trend for resistivity against diameter for a solid cylinder. This is because MWCNTs are not solid cylinders and the addition of walls does not increase the cross sectional area in a linear manner.

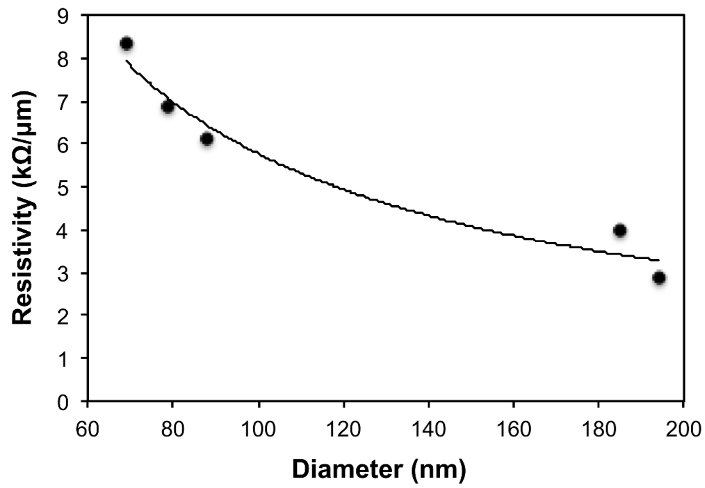


Figure 5. Plot of resistivity against diameter for Ar ion bombarded MWCNT.

In summary, two-point probe and Raman spectroscopy has been used to investigate the effects of cleaning, by vacuum annealing and argon bombardment, on the conduction characteristics of MWCNTs. It has been found that surface contamination has a large effect on the two-point probe conductivity measurements resulting in inconsistent and non-reproducible contacts. Furthermore, surface contamination also increases the electric field strength at the probe⋯CNT contact causing increased band bending. This results in a very high resistance (100 times that of the MWCNTs) due to overlapping depletion regions when probe separations are small (< 4 µm). We believe that this give a plausible explanation as so why there is such a range of resistivities reported in the literature.[6]

It was observed that annealing at both 200 °C and 500 °C reduced the surface contamination on the MWCNT without changing the concentration of defects present. However, remaining surface contamination caused high resistance probe⋯CNT contacts, which still did not allow intrinsic conductivity measurements of the MWCNTs. It was observed that the high resistance measured due to the overlapping depletion regions occurred at lower probe separations for the CNTs heated to 200 °C when compared to the untreated sample; however, this was not observed at 500 °C. This observation also presents new exciting possibilities for CNT device creation. Currently contact type is controlled by using process heavy techniques to modify the material properties, such as doping, however, our result suggest the contact type can be controlled using the placement of contacts. Our result also demonstrates for the first time the importance of removing surface contamination to avoid resistance channels when making nanoscale devices.

Argon bombardment reduced the surface contamination more than vacuum annealing at 500 °C but caused a slight increase in the defects concentration. Argon bombardment was sufficient to remove enough surface contamination to make measurements from which the resistivity of the MWCNT could be calculated. It was found that resistivity was of the order of kΩ and dependent on the diameter of the nanotubes, with thicker tubes displaying lower resistance values. From our results it is clear that for consistent conductivity data of MWCNT (or indeed SWCNT), surface cleaning is required in order to make reproducible and consistent contacts. This may be also an issue where good CNT···CNT contacts are required in CNT fibers.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the http://pubs.acs.org. Additional I/V plots for MWCNTs before and after heating to 200 °C, 500 °C and Ar ion bombardment.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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