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Assessing and ameliorating the influence of the electron beam on carbon nanotube oxidation in environmental transmission electron microscopy

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Abstract

In this work, we examine how the imaging electron beam can induce damage in carbon nanotubes (CNTs) at varying oxygen gas pressures and electron dose rates using environmental transmission electron microscopy (ETEM). Our studies show that there is a threshold cumulative electron dose which brings about damage in CNTs in oxygen – through removal of their graphitic walls – which is dependent on O₂ pressure, with a 4–5 fold decrease in total electron dose per decade increase at a lower pressure range (10^{−6} to 10^{−5} mbar) and approximately 1.3 –fold decrease per decade increase at a higher pressure range (10^{−3} to 10⁰ mbar). However, at a given pressure, damage in CNTs was found to occur even at the lowest dose rate utilized, suggesting the absence of a lower limit for the latter parameter. This study provides guidelines on the cumulative dose required to damage nanotubes in the 10^{−7} mbar to 10⁰ mbar pressure regimes, and discusses the role of electron dose rate and total electron dose on beam-induced CNT degradation experiments.

Keywords

environmental transmission electron microscopy; oxidation; electron dose; carbon nanotubes; beam damage

1. Introduction

In situ transmission electron microscopy (TEM) concerns real time observations, such as material reactions at the atomic level. The biggest contribution to the growth of this field in recent years is in the control of the specimen environment, such as liquid or gas [1, 2], owing to developments in specialized specimen holders [3–7] as well as advances in instrumentation, including aberration correction [2, 8–10]. Environmental TEM (ETEM) is the latter approach whereby the microscope is modified to include fixed apertures and a

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differentially pumped vacuum system so as to support the introduction of gases into the otherwise high vacuum of the TEM [10–12].

In ETEM experiments, the incident electron beam undergoes additional scattering from having to traverse the gas molecules that surround the specimen, which leads to reduction in image intensity and resolution [13–17]. Furthermore, gas molecules are also ionized by the incident electron beam which leads to artifacts and affects experimental outcomes. Our earlier studies concerning oxidation of carbon nanotubes (CNTs) in the ETEM have shown that CNTs which were heated in an O₂ gas environment in the absence of the electron beam oxidize at the side walls, starting from the outermost wall [18]. There is no visible oxidation by exposing the CNTs to oxygen at room temperature, and the degree of attack increases as the temperature is raised from 300 °C to 400 °C and 520 °C, which is consistent with a thermally activated process. Unlike what had been reported previously based on *ex-situ* oxidation [19, 20], tube caps are not found to oxidize preferentially [18, 21]. However, when the imaging electron beam was illuminated in the presence of O₂ gas at room temperature, beam induced ionization of gas molecules led to rapid etching and destruction of CNTs at both caps and side walls [22]. This same behavior was also observed when an inert gas (N₂) was used in place of O₂ [22].

Unequivocal *in situ* ETEM observations require a thorough understanding of the influence of the electron beam and establishing protocols to eliminate beam-induced artifacts. The effects of electron dose rate [23–25], total electron dose [22, 25], and beam on / beam off [18, 26] on gas-solid reactions have been reported. We had previously quantified the influence of the imaging electron beam by establishing the cumulative electron dose required to cause onset of visible damage in the CNTs, and showed that there is a two orders of magnitude difference in this parameter to oxidize / damage CNTs in 10^{−7} mbar (high vacuum) versus that in approximately ~ 10⁰ mbar O₂ [22]. In the present work, we examine the effect of the electron beam on carbon nanotube oxidation behavior using lower O₂ pressures (10^{−6} mbar to 10^{−1} mbar) and at varying dose rates. This is important in assessing the vacuum conditions for prolonging the life of CNTs during their major application as field emission sources. A careful quantitative assessment has not been done before for CNT oxidation. This study provides guidelines on the cumulative dose required to damage nanotubes in the 10^{−7} mbar to 10⁰ mbar O₂ pressure regimes, and discusses the role of electron dose rate and total electron dose on beam-induced CNT oxidation experiments.

2. Experimental Procedures

2.1 Sample synthesis and preparation

Arc-discharged synthesized carbon nanotubes (CNTs) were used in this study [27]. TEM samples were prepared by suspending the nanotubes in ethanol via sonication, and drop-casting the samples on 300-mesh molybdenum TEM grids with holey carbon support film (Pacific Grid-Tech).

2.2 ETEM studies

All experiments were performed using an image spherical aberration (Cs) corrected 80–300 Titan environmental TEM (ETEM) (FEI Company) operated at 80 kV, which is believed to be below the threshold energy for knock-on damage in single-walled CNTs [28]. Several authors including ourselves have reported CNT damage upon prolonged exposure to an 80 keV illuminating beam, which might arise from the exact structures of different CNTs at their caps and side wall chiralities, or due to less pure vacuum conditions than in our instrument [29–31]. Our data at 80 kV therefore represents a baseline for comparing the results under different oxygen pressure and dose rates. The microscope is equipped with a differentially pumped vacuum system to support the environmental mode of up to 10 mbar gas pressure. The SuperTwin objective lens pole pieces (with a gap of 5.4 mm) function as the environmental cell [14]. It is fitted with an Edwards barocell 600 capacitance manometer (BC/O) and a Pirani Penning gauge (PP/O) which measure the gas pressure in the sample chamber (octagon) during a gas experiment. The BC/O readout is gas independent and shows a valid readout for pressures from ~ 0.5 mbar to 10 mbar. The PP/O is gas-dependent and has been calibrated for nitrogen. At pressures below 0.5 mbar, the actual pressure readout in the microscope chamber was obtained using the PP/O readout. In the high pressure range (0.5 mbar to < 10 mbar), the BC/O measurement was used. The presence of O₂ in the ETEM was verified using the residual gas analyzer with which the microscope is equipped, as well as electron energy loss spectroscopy (EELS) [18].

The studies were carried out at room temperature, with specimens mounted in a single tilt holder. The anticontamination blade (cold finger) was cooled with liquid nitrogen to minimize hydrocarbon contamination. Research grade (99.9999%) purity O₂ gas (AirLiquide Inc.) was introduced into the microscope column by a homemade portable mixing gas console which consists of three input mass flow controllers (MFCs) that can accurately mix up to three different high purity gases, and one output MFC which is connected to the ETEM gas inlet (Fig. 1). A single gas input source (oxygen) was used in this study.

First, control experiments were established at room temperature by blanking the electron beam whenever oxygen was flowing inside the column octagon. Aberration-corrected (ACTEM) images of the CNTs were acquired in high vacuum (ca. 1×10^{-7} mbar) at the start of the experiment. Then, the column valves were closed and quasi *in situ* oxidation of CNTs was performed with the beam blanked and by introducing ~ 1.7 mbar of oxygen into the column octagon for 15 min. The oxygen was then purged from the octagon, and the column valves were re-opened only after the high vacuum condition of the microscope had been restored. The same nanotubes were located and imaged to identify any differences after having been exposed to oxygen [18]. The samples underwent three cycles of molecular oxidation using this beam blanking approach.

To investigate the effects of the electron beam on CNTs with oxygen in the ETEM, suitable areas of the sample were first located and imaged in high vacuum. Then, the column valves were closed and oxygen was introduced into the microscope column. A combination of input MFC flow rate and microscope leak valves was used to adjust the gas flow to achieve the desired O₂ pressure range of 10^{-6} mbar to 10^{-1} mbar. The PP/O readout was monitored

and once the gas pressure stabilized, the column valves were opened, and *in situ* TEM recordings of the identified nanotube were made using a CMOS-based OneView camera (Gatan Inc.) operated in a 2k-by-2k pixel setting and at frame speeds between 5 and 20 frames per second (fps). The electron dose rate, measured in units of number of electrons per square Ångström per second ($\text{e}/\text{\AA}^2\cdot\text{s}$), was also noted for each recording. This parameter had been calibrated using a TEM holder with a Faraday cup. This procedure was repeated at pressures ranging from $\sim 10^{-7}$ mbar to 10^{-1} mbar, and at varying electron dose rates of ~ 60 $\text{e}/\text{\AA}^2\cdot\text{s}$ to 4000 $\text{e}/\text{\AA}^2\cdot\text{s}$. The illumination conditions were varied by changing the second condenser lens current (intensity) of the ETEM. The data were analyzed and the time to damage the CNTs in each case was noted. In the literature, the terms electron dose rate and beam current density are used interchangeably. The latter has units of Amperes per unit area, with a conversion factor of $1 \text{ A}/\text{cm}^2 \equiv 620 \text{ e}/\text{\AA}^2\cdot\text{s}$.

3. Results and Discussion

3.1 Electron beam blanking (control) experiments

Fig. 2 shows a representative TEM image of the carbon nanotubes that were investigated in this work. The image was acquired under high vacuum (10^{-7} mbar) conditions. For the best image resolution, CNTs which extend over the through-hole (vacuum) regions of the grid were studied. Higher magnification, aberration-corrected TEM (ACTEM) images of CNTs A, B, C and D are presented in Fig. 3a(i), b(i), c(i) and d(i). Fig. 3a(ii), b(ii), c(ii) and d(ii) are the same nanotubes imaged in high vacuum after having been exposed to 1.63 mbar of oxygen for 15min with the electron beam blanked. Images in panels (iii) and (iv) of Fig. 3 show the nanotubes after they had been further exposed to 1.77 mbar and 1.69 mbar of oxygen respectively in the ETEM, for 15min each time, with the column valves closed during oxygen exposure. Apart from the removal of the amorphous carbonaceous overcoat of the CNTs in some instances, there is no apparent change in the structure of the nanotubes after the three oxidation cycles. This outcome is expected, as graphite and oxygen are known to not react with each other at room temperature whereas the estimated knock-on threshold energy for amorphous carbon is 30 keV [32].

3.2. Electron beam irradiation experiments

The situation is different when the electron beam illumination is maintained during O_2 gas flow. Fig. 4 shows a nanotube imaged (a) under high vacuum at the start of the experiment and (b) after having been exposed to 3.03×10^{-3} mbar of O_2 for 30 s with the beam on, using an electron dose rate of $1170 \text{ e}/\text{\AA}^2\cdot\text{s}$. Visible damage is observed at both its tip and side wall, as indicated by the arrows in Fig. 4(b). This is in contrast to the oxygen beam blanking experiments whereby there is no change in the nanotubes structures. We had attributed this increased reactivity to gas ionization from the electron beam and momentum transfer from the O_2 molecules and O_2^+ ion species to the CNTs, with the positive ion species attracted to the nanotubes via image forces with effective field lines concentrated at their tips [22].

The O_2 gas pressure has a direct impact on the time to damage CNTs, with the CNTs withstanding longer periods of time at lower O_2 pressures before the removal of their

graphitic walls in the ionizing gas environment. Fig. 5 documents the changes in another nanotube during exposure to the electron beam under O₂ gas pressure of 1.1×10^{-5} mbar, which is two orders of magnitude lower compared to that reported in Fig. 4. Utilizing a lower pressure, the time to cause onset of visible damage in the nanotube is increased by a factor of about three, from ~ 30s to ~ 100s, in spite of a higher electron dose rate (another parameter which we will discuss later) of $3290 \text{ e-}/\text{\AA}^2\cdot\text{s}$ being used.

Previously, we had noted that structural changes can also occur in CNTs imaged under high vacuum ($\sim 10^{-7}$ mbar) at 80 kV after long periods of continuous electron beam irradiation. Similar findings were also observed in this work. Fig. 6 shows two CNTs imaged in high vacuum using electron dose rates of (a) $1050 \text{ e-}/\text{\AA}^2\cdot\text{s}$ and (b) $276 \text{ e-}/\text{\AA}^2\cdot\text{s}$. The images are acquired with exposure times of 0.15 sec and 0.2 sec, respectively. The first nanotube (Fig. 6(a)) remains unchanged following 60 min of continuous electron beam irradiation (Fig. 6a(ii)). However, the second nanotube (Fig. 6b) was observed to have its outermost wall broken after 53min of electron beam illumination, as indicated by the arrow in Fig. 6b(ii). This damage that we see in the absence of O₂ might be due to secondary damage (for example, displacement of H atoms that, in turn, displace C atoms). These secondary displacements depend on the cleanliness of the specimen and the TEM column, but we believe at present that they are due to the electron beam itself.

The influence of the electron beam on CNT damage at different O₂ pressures was quantified by plotting the cumulative electron dose (the product of the electron dose rate and the time taken to cause visible damage) versus O₂ pressure and is shown in Fig. 7. A total of 130 datasets were analyzed. There is a wide range of onset values at any given pressure, which may be related to the actual structure or defects of individual CNTs. This is a factor which we did not investigate further but which is a phenomenon clearly worthwhile to clarify. Table 1 shows the median cumulative electron dose for each order of magnitude of O₂ pressure. The number of electrons (per areal density) required to damage CNTs decreases with increasing pressure. At lower (10^{-6} to 10^{-5} mbar) O₂ pressures, there is a 4–5 -fold decrease in electron dose per decade increase in pressure whereas at higher (10^{-3} to 10^0 mbar) O₂ pressures the decrease is 1.3 -fold per decade. The cumulative electron dose can vary by about an order of magnitude within each order of magnitude of O₂ pressure. We attribute this variation in data spread to be due to the non-uniform nature of the nanotubes.

Next, we examine the effect of electron dose *rate* on the time to cause onset of CNT damage. Fig. 8 shows a time series of TEM images from three CNTs acquired under O₂ pressures of $(1.66 \pm 0.5) \times 10^{-4}$ mbar and electron dose rates of (a) $2880 \text{ e-}/\text{\AA}^2\cdot\text{s}$, (b) $1960 \text{ e-}/\text{\AA}^2\cdot\text{s}$ and (c) $740 \text{ e-}/\text{\AA}^2\cdot\text{s}$, respectively. Panels (i) of Fig. 8 shows the nanotubes at the start of the experiment (in high vacuum), and panels (ii) to (v) correspond to images extracted at 30s, 60s, 90s and 120s of the recordings. The first CNT (Fig. 8a) which had been exposed to the highest electron dose rate shows breakage of walls located on its right kink by 60s, as indicated by the arrow in Fig. 8a(iii). The recordings reveal that damage had started at 44 sec. The location of breakage – the kink – is one which would cause electric field lines to be concentrated, and is consistent with our earlier hypothesis about image force effects being the cause of damage [22]. It may also be related to the pentagonal carbon rings necessary at these locations to give rise to the curvature. The nanotube in Fig. 8(b) which was recorded

using an electron dose rate of $1960 \text{ e}^-/\text{\AA}^2\cdot\text{s}$ shows changes in its cap structure starting at 60 s (Fig. 8b(iv)), which become more apparent by 90 s (Fig. 8b(v)). Finally, for the CNT which had been illuminated using the low dose rate of $740 \text{ e}^-/\text{\AA}^2\cdot\text{s}$, side wall damage was observed at $\sim 120 \text{ s}$ (Fig. 8c(v)). The results suggest that operating at lower dose rates can prolong observation times before the onset of specimen damage. However, damage was found to occur even for the lowest dose rate (down to $\sim 60 \text{ e}^-/\text{\AA}^2\cdot\text{s}$) which we used in this work.

Another observation arising from electron beam illumination during O_2 gas flow is the perturbation of the amorphous carbon overcoat surrounding the CNTs. At lower O_2 pressures (10^{-5} mbar to 10^{-3} mbar), the presence of electron beam and O_2 gas induces mobility of the amorphous carbon which increases with pressure but the time to remove both the amorphous and graphitic carbon is longer compared to operating at higher O_2 pressures ($10^{-1} - 10^0 \text{ mbar}$). In the latter, there was rapid removal of both amorphous and CNT structures [22] due to a larger number of gas molecules being present ($\sim 10^{15}$ at 1 mbar versus $\sim 10^{11}$ at 10^{-4} mbar under room temperature and assuming a cube volume with edges equal to objective pole piece gap) and the higher flow rates (number of molecules per unit area per unit time) associated with operating at higher pressure.

By examining the behavior of CNTs at each electron dose rate and pressure, and noting their time to damage, we plot a graph of cumulative electron dose versus electron dose rate for various O_2 pressures and this is shown in Fig. 9. Four pressure ranges were analyzed, namely (i) $(1.0-3.0) \times 10^{-7} \text{ mbar}$ (high vacuum) (black stars), (ii) $(1.0-3.0) \times 10^{-5} \text{ mbar}$ (green squares), (iii) $(1.0-3.0) \times 10^{-4} \text{ mbar}$ (red circles) and (iv) $(1.0-3.0) \times 10^{-3} \text{ mbar}$ (blue triangles). The data points are fitted to a first order polynomial. An upper limit of cumulative dose of $> 1.5 \times 10^6 \text{ e}^-/\text{\AA}^2$ was assigned in the vertical axis because damage in CNTs under high vacuum (if any at all) tends to occur only after fairly long exposure times (about 60 min or longer) and so these experiments are usually terminated when no change is observed after prolonged beam illumination. The lines of best fit suggest that there is little change in the cumulative electron dose as the electron dose rate is varied. At a given pressure, CNTs exposed to O_2 gas with an illuminated beam can withstand a threshold cumulative dose below which no observable damage occurs. The relative insensitivity of damage to dose rate is thought to be related to the lifetime of the limited O_2^+ species [22]. Once created by the fast electron beam, there is no straightforward mechanism whereby the missing electron is replaced. Accordingly, increasing the dose rate is not creating a higher proportion of the O_2^+ species whereas the total dose is.

We also considered the possibility of damage due to beam heating at increasing dose rates. Several studies have reported that during a typical TEM experiment, the sample is not necessarily heated up significantly by the electron beam [33–35]. Because of the thin nature of the CNTs and their good thermal conductivity, we do not think that there will be a substantial rise in temperature brought about from increasing dose rate, and that the increased ionization level of the gas environment is a stronger effect. Furthermore, the dose rates that were applied in our experiments were at least an order of magnitude lower than those reported in [35] for imaging single layer graphene, and as can be seen in Figure 9, the

influence of increasing dose rate is rather minimal, and is small compared to that of overall dose.

In the literature, electron beam damage has been assessed both in terms of electron dose rate and total dose. Jiang and Spence investigated beam damage in silicate glass under high vacuum using time-dependent EELS and found a threshold dose rate below which the damage involving the formation of O defects was not detected [36]. Using ETEM, Simonson et al. [23] studied Pt/Al₂O₃ catalysts and observed shrinkage in the catalyst particles which they attributed to a combination of the electron beam current density (i.e. dose rate) and an oxidizing gas environment. The effect of the electron beam was mitigated using a low dose rate for which the accumulated beam-induced shrinkage is comparable with or smaller than the image pixel size [23]. Kuwauchi and coworkers studied the intrinsic structure of gold nanoparticles on TiO₂ support under high vacuum, O₂ and 1% volume CO/air, and showed that both electron dose rate and total electron dose influence the morphology of the specimen over time [25]. On the other hand, the low dose technique [37] used in biological and organic materials is based on the idea of a threshold (total) dose, also known as critical dose [38] or characteristic dose [39], below which beam damage is negligible. In this work, damage in CNTs was found to occur for the lowest dose rate of $\sim 60 \text{ e}^-/\text{\AA}^2\cdot\text{s}$, which we utilized that was still suitable for high-resolution imaging, after approximately 10 min. However, we are able to derive a threshold *cumulative dose* at a given O₂ pressure below which damage does not occur (Table 1). The cumulative dose dependency that we observe parallels that of ion implantation processes (for example of Si in GaN) whereby the total dose of the implanted ions plays a more significant role in influencing the structure [40]. In metals studied using high voltage electron microscopy (HVEM), dose rate appears to be to be important because of the diffusive nature of the displaced atoms returning to the created vacancies [41]. However, the formation of visible defect clusters in thin Cu foils was only observed above a threshold irradiation dose with 650 keV electrons at 10 K, suggesting the significance of cumulative dose as well [42].

There are a few aspects which are not addressed in this present work but will be interesting to follow up in a future report. For example, high-vacuum studies concerning electron scattering and beam-induced damage mechanisms of CNTs and related carbon materials at varying acceleration voltages which had been reported in [34,43] can be extended to reactive gas environments. In this study we have attributed the variation in cumulative electron dose required to cause damage to the non-uniform nature of the nanotubes. There did not appear to be any obvious role of CNT defect structure apart from the highly curved regions of the cap, on the location of the initial damage, based on all the images we have analyzed. This study can be expanded in the future to include analyses of the local structure of the CNT and defects in the hexagonal carbon atom array, and correlating the reactivity of the nanotubes to their local structure, as Liu et al. [44] had done to correlate reactivity of single-walled CNTs to diameters, chirality and metallicity.

4. Summary and Conclusions

In summary, this work discusses damage in CNTs from electron beam illumination in an O₂ gas environment using environmental transmission electron microscopy. The studies show

that there is a threshold cumulative electron dose required to damage CNTs – through removal of their graphitic walls – which is dependent on O₂ pressure. Damage is less at lower pressures, decreasing by as much as five-fold per decade at low pressure. There is no apparent lower limit to the electron dose rate at which nanotubes will not be destroyed. Therefore, the only way to mitigate the influence of the imaging beam is to operate at cumulative dose not exceeding the threshold for a given O₂ pressure, through interplay of beam illumination and accumulated exposure time. This is important for the strategy and interpretation of *in situ* studies of carbon nanotube oxidation. It has also been found that the structural damage to carbon nanotubes in oxygen under active field emission conditions is similar to that under TEM *in situ* observations [45] and so it is clear that the operating lifetime of field emitting CNTs is extended significantly at lower background partial oxygen pressures, in agreement with field emission measurements [46]. This is important for their practical application as field emission sources.

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Highlights

- In environmental transmission electron microscopy (ETEM) experiments, gas molecules can be ionized by the incident electron beam which lead to artifacts and affect experimental outcomes.
- We show how the electron beam can induce damage in carbon nanotubes at varying oxygen gas pressures and electron dose rates using environmental transmission electron microscopy (ETEM).
- We find that there is a threshold cumulative electron dose required to damage CNTs –through removal of their graphitic walls – which is dependent on O₂ pressure.
- However, at a given pressure, damage in CNTs was found to occur even at the lowest dose rate utilized, suggesting the absence of a lower limit for the latter parameter.

Figure 1.
Photograph of the gas mixing console beside the ETEM.

Figure 2.
Representative low-magnification TEM image of arc discharge carbon nanotubes.

Figure 3.

Aberration-corrected TEM images of nanotubes (a) A, (b) B, (c) C and (d) D, which had been identified in Figure 2, at the start of the experiment (panel i), and after exposure to 1.63 mbar (panel ii), 1.77 mbar (panel iii) and 1.69 mbar (panel iv) of oxygen for 15 min per exposure at room temperature. The electron beam was blanked when oxygen was introduced into the ETEM. There is no change in the structure of the CNTs after three room temperature oxidation cycles. All images were acquired under high vacuum.

Figure 4.

A nanotube (a) at the start of the experiment in high vacuum, and (b) after being exposed to the electron beam for 30 s in 3.03×10^{-3} mbar O_2 . Scale bars equal 10 nm.

Figure 5.

A nanotube (a) at the start of the experiment in high vacuum, and (b) after being exposed to the electron beam for 100 s in 1.1×10^{-5} mbar O_2 . The curved cap of the nanotube was damaged from the continuous electron beam illumination in O_2 after 100 s. Scale bars equal 5 nm.

Figure 6. Electron beam illumination of carbon nanotubes in high vacuum (10^{-7} mbar) and a dose rate of (a) $1050 \text{ e}^-/\text{\AA}^2\cdot\text{s}$ and (b) $276 \text{ e}^-/\text{\AA}^2\cdot\text{s}$. Scale bars equal 5 nm.

Figure 7. Cumulative electron dose (logarithmic scale) to damage carbon nanotubes by continuous 80 kV electron beam illumination as a function of O₂ pressure at room temperature.

Figure 8.

Structural changes in carbon nanotubes under dose rates of (a) $2880 \text{ e}^-/\text{\AA}^2\cdot\text{s}$, (b) $1960 \text{ e}^-/\text{\AA}^2\cdot\text{s}$ and (c) $740 \text{ e}^-/\text{\AA}^2\cdot\text{s}$ in $\sim 10^{-4} \text{ mbar O}_2$ (actual pressure on the left of each dataset). The first column (panels i) show the nanotubes at the start of the experiment under high vacuum, and panels (ii) to (iv) are recorded at 30 s, 60 s, 90 s and 120 s at the given O_2 pressure. Scale bars equal 5 nm.

Figure 9.

Cumulative electron dose versus electron dose rate, for datasets corresponding O₂ pressures (i) $(1.0 - 3.0) \times 10^{-7}$ mbar (high vacuum) (black stars), (ii) $(1.0 - 3.0) \times 10^{-5}$ mbar green squares), (iii) $(1.0 - 3.0) \times 10^{-4}$ mbar (red circles) and (iv) $(1.0 - 3.0) \times 10^{-3}$ mbar (blue triangles). The data points are fitted to a first order polynomial.

Table 1

Median cumulative dose required to damage CNTs for each decade of O₂ range starting with the stated value investigated in this study.

O ₂ pressure (mbar)	Cumulative dose to damage CNTs (e-/Å ²)
10 ⁻⁷	1.5 × 10 ⁶
10 ⁻⁶	3.2 × 10 ⁵
10 ⁻⁵	8.6 × 10 ⁴
10 ⁻⁴	5.8 × 10 ⁴
10 ⁻³	2.5 × 10 ⁴
10 ⁻²	1.9 × 10 ⁴
10 ⁻¹	1.5 × 10 ⁴
10 ⁰	1.2 × 10 ⁴