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Electron irradiation-induced destruction of carbon nanotubes in electron microscopes

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Abstract

Observations of carbon nanotubes under exposure to electron beam irradiation in standard transmission electron microscope (TEM) and scanning electron microscope (SEM) systems show that such treatment in some cases can cause severe damage of the nanotube structure, even at electron energies far below the approximate 100 keV threshold for knock-on damage displacing carbon atoms in the graphene structure. We find that the damage we observe in one TEM can be avoided by use of a cold finger. This and the morphology of the damage imply that water vapour, which is present as a background gas in many vacuum chambers, can damage the nanotube structure through electron beam-induced chemical reactions. Though, the dependence on the background gas makes these observations specific for the presently used systems, the results demonstrate the importance of careful assessment of the level of subtle structural damage that the individual electron microscope system can do to nanostructures during standard use.
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1. Introduction

Transmission electron microscopes (TEM) and scanning electron microscopes (SEM) are standard tools, not only for imaging nanostructures, but also fundamental for the creation and investigation of nanodevices using electron beam lithography (EBL), electron beam deposition [1], or in situ nanomanipulation [2]. Several publications have described irradiation-induced structural changes in carbon structures [3], such as single- and multi-walled carbon nanotubes, SWNT [4] and MWNT [5], respectively, and in the presence of water vapour inside an environmental SEM (ESEM) [6]. Such induced damage to the nanostructures during electron microscope investigation is naturally a serious problem for the operation of these instruments, but can at times be an advantage when used to modify the structures at the nanoscale [6].

Several studies of electron irradiation-induced damage and the dependence on beam energy and irradiated dose have been published. They can be divided into physical and chemical effects. The physical 'knock-on damage' in which direct electron collision with atoms causes a change in the crystal structure or the removal of an atom, has a threshold at beam energy of about 80 keV for SWNT [4]. The disordering is attributed to $sp^2 \rightarrow sp^3$ transitions of the carbon atoms, causing cross-linking between adjacent planes in a nanotube. Chemical damage to nanotubes caused by irradiation induced reactions are mainly known from electron beam induced deposition of a carbonaceous layer from vacuum pump oils and other contaminants present in vacuum systems. However, depending on the type of background gas, the inelastic electron collisions can

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cause either deposition, when for instance hydrocarbons are present [7], or etching if gasses such as water or oxygen are present [6,8]. It has been observed that water enclosed in the interior of a nanotube can cause etching holes in the MWNT structure if irradiated by a sufficiently intense electron beam in a TEM [9,10].

By introducing water vapour as a background gas in an ESEM it has been demonstrated that the water induced chemical reactions can be used to cut nanotubes in sections [6], while the introduction of carbonaceous compounds in an ESEM with water vapour may also cause deposition [11]. The etching can be caused by the reaction $C + 2H_2O \rightarrow CO_2 + 2H_2$ with $\Delta H = -82.4\,kJ/mol$. In addition to this water reaction, carbon can be removed from the nanotube structure by the exothermic reactions $C + O_2 \rightarrow CO_2$ and $C + \frac{1}{2}H_2 \rightarrow CH$. Both oxygen and hydrogen can be present in the vacuum chamber, or adsorbed on the nanotube, and in the case of hydrogen, also released from the water reaction.

The investigation presented in this paper was carried out in order to ensure that no damage would be caused by the electron irradiation during repeated SEM [2,12], and TEM [13] imaging of nanotube devices used for nanomanipulation and electrical measurements. The surprising result naturally relates to the specific SEM and TEM instruments used in this study, and to some extent also on the instrument usage history since introduction of sufficient carbonaceous contamination of the specimen chamber will result in electron beam-induced deposition. This paper hence mainly serves as a demonstration of the need for careful attention to the level of nanostructure damage during imaging in the individual electron microscope system, especially when no electron beam-induced deposition is observed. The damage can be subtle and not readily observed in SEM.

For the present study, we used a Philips EM 430 TEM operated at 100 keV. We found that using low-beam currents considerably improved the imaging conditions and resulted in lower damage rates than high-beam currents. To study the damage effect we used high current densities. The beam current cannot readily be measured in the TEM, but an upper order of magnitude estimate of the beam current density must be $j_{max} = 10^3\,A/cm^2$ (assuming $0.1\,\mu A$ beam current at the condenser lens setting "spot 2" and a beam area of approximately $0.01\,\mu m^2$ at high magnification). The SEM was a LEO 1550 with a turbo pumped vacuum system.

2. Damage observed during TEM imaging

The TEM image sequence in Fig. 1 shows a multi-walled carbon nanotube slowly being destroyed by the electron beam exposure. After 15 min at high-beam current the nanotube structure has been completely removed. Even very large multi-shell MWNT, as the one shown in Fig. 2, can be considerably damaged by prolonged exposure to the beam.

From the cross section of both the small (Fig. 1) and large nanotube (Fig. 2), it seems that a considerable fraction of the outer shells has been removed, while the inner shells apparently are less susceptible to the observed irradiation-induced damage. Irradiation-induced cross-linking of the carbon bonds would be expected to appear throughout the nanotube and convert the shell structure to amorphous carbon. Knock-on collisions are expected to mainly attack graphene planes perpendicular to the beam, and the damage seems to be considerable to the planes parallel to the beam in the outer shell. The nanotube does not collapse as reported in an 800 kV TEM experiment [14]. In both nanotubes (Figs. 1 and 2), the damage to the outer shells could be interpreted as the formation of pits in the structure. Such pits are known to form by oxidation [15], which would also explain why material appears to be removed from the nanotube surface, and not in a uniform manner throughout the nanotube. The question is then what causes oxidation in the vacuum environment.

A plausible explanation for the observed damage to the MWNT is that etching is taking place on the outer shell, activated by the electron irradiation. The etching agent could be oxygen, water, hydrogen, or unknown compounds adsorbed on, or absorbed within the MWNT shells. It appears unlikely that absorbed compounds within the nanotube should cause the damage, since the effect appears to occur mainly at the surface. Oxygen and water vapour are abundant in ambient conditions before loading the sample. Especially water could be adsorbed on the sample holder in air and in this way be transferred to the TEM chamber. A leak in the TEM vacuum system could in principle also increase the water and oxygen vapour pressure in the TEM vacuum system, but the vacuum was in fine condition during the experiments (unfortunately a EM 430 TEM does not have a calibrated pressure gauge).

Since the damage primarily attacks the outer shells, single wall nanotubes (SWNT) would probably be highly sensitive to the effect. This was tested experimentally: A lacy carbon grid was dipped into a sonicated isopropanol dispersion of HiPCO SWNTs [16]. The grid was dried and it was attempted to acquire high-resolution TEM (HRTEM) images of the SWNTs. Fig. 3a,b shows a low-resolution TEM image of the SWNT sample before and after the attempt to image at high resolution. It turned out to be impossible to achieve high-resolution images of the SWNT as they practically disappeared as the beam was focused on them. Considering the damage rates reported in literature at high irradiation doses [4,17], it is tempting to believe that the observed behaviour is due to knock-on collisions with the high-current density in the beam. This however cannot be the case since it is not observed in the subsequent experiments made when using the TEM cold finger. The TEM is equipped with a cold finger that can be cooled by liquid nitrogen, allowing plates above and below the specimen holder to reach temperatures low enough to condense water and carbohydrates within the vacuum chamber without cooling the sample. A cold finger is

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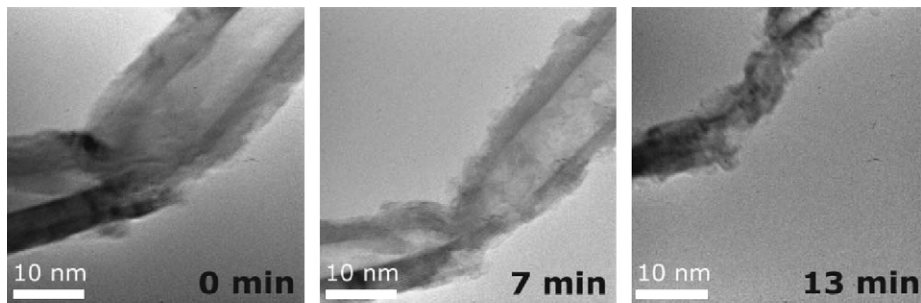

Fig. 1. TEM image sequence showing the progressive destruction of the carbon shell structure with respect to time under intense electron beam irradiation.

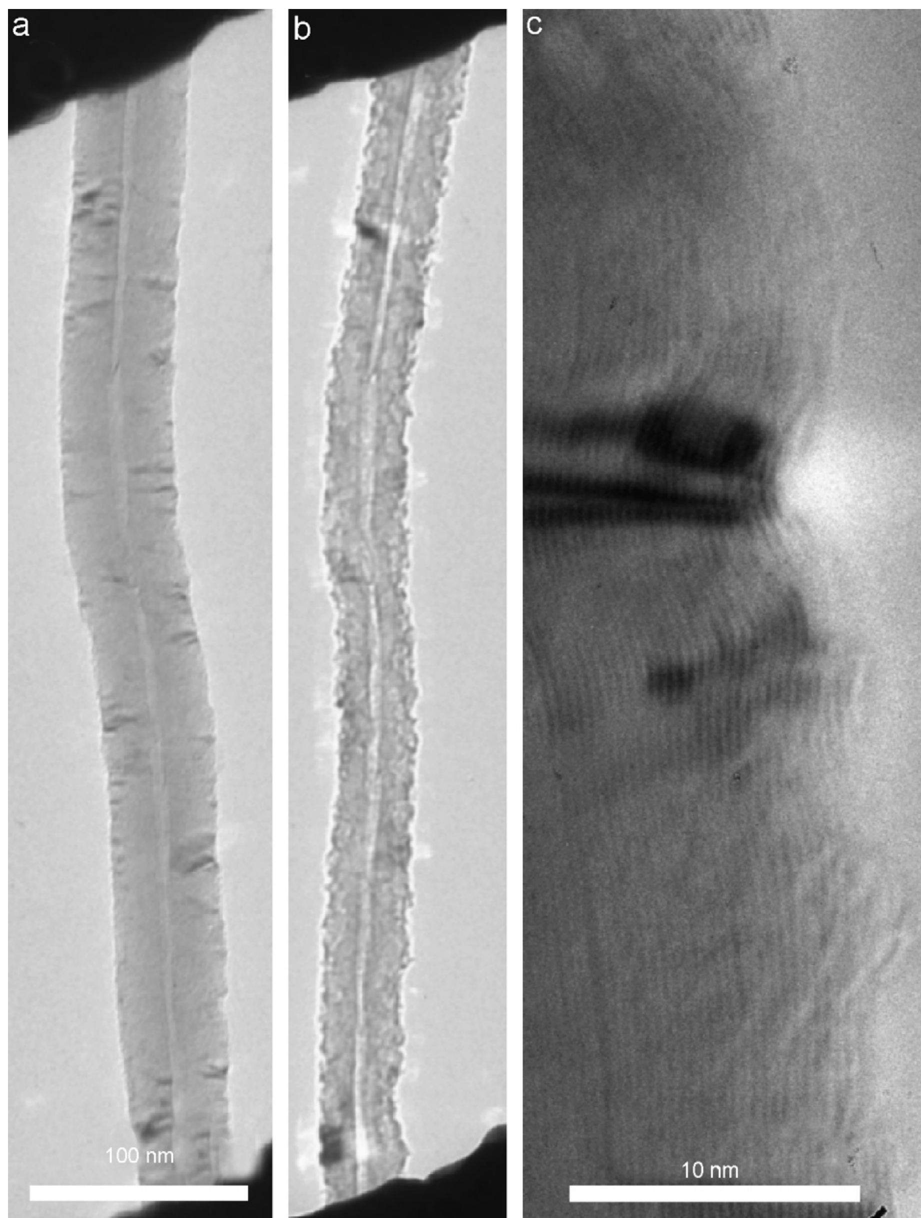

Fig. 2. Irradiation damage of a large C-MWNT. (a) The initial overview image of the suspended C-MWNT in the setup presented in Ref. [13]. (b) The same tube after extensive imaging at high resolution with a focused beam. The inner shell structure appears relatively unaffected, while the outer structure has been severely damaged. (c) Close-up of the outer shell structure, illustrating how regions with bent shell structure cause the dark regions visible in the overview images. The inner shells are fairly intact, while the outer shells appear severely damaged.

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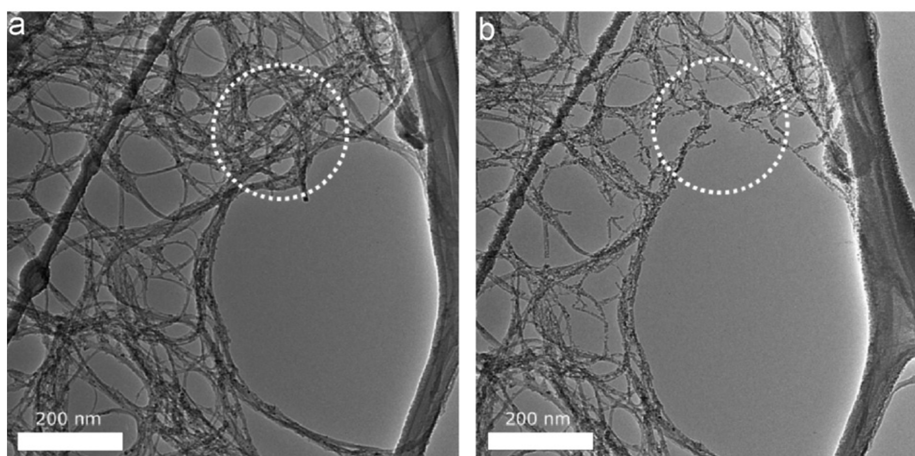

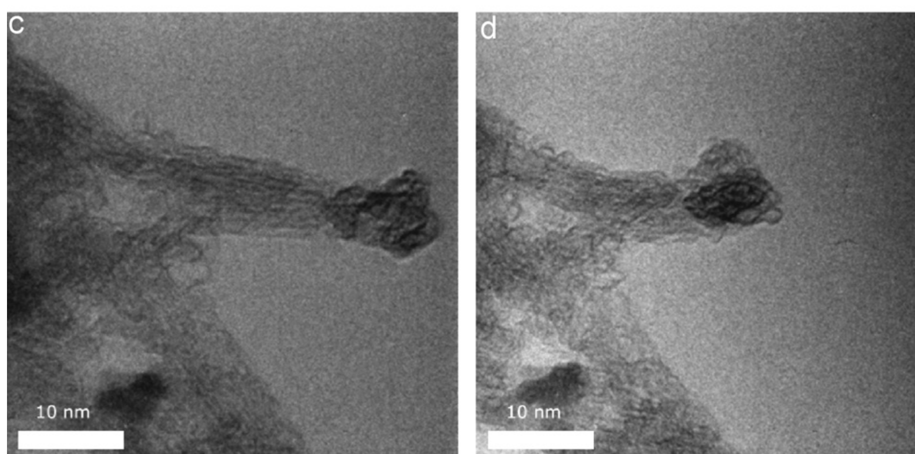

Fig. 3. The irradiation induced damage rate and the type of damage depends on the cold finger temperature. (a, b) HRTEM was attempted on a lacy carbon grid with SWNTs without cooling the cold finger. As the beam was focused to achieve a higher magnification, the SWNTs were seen to disappear rapidly. About 30 min of irradiation mainly in the encircled region lead to the removal of a large fraction of the exposed SWNT sample. (c, d) Cooling the cold finger with liquid nitrogen made it possible to acquire an image at high magnification. Image (c) and (d) show the same sample before and after 14 min of exposure to the focused beam at high magnification. Without cooling, focusing would not have been possible and such a small structure would have disappeared in a couple of minutes. Little, if any, material is removed during the 14 min exposure with cooling. The change in the SWNT structure with cooling is probably mainly due to reordering rather than removal of the carbon atoms.

normally used for condensing carbohydrates to avoid electron beam deposition in the TEM. Water has a vapour pressure of 10^{-8} Pa at $-100\,^{\circ}$C, and even lower at liquid nitrogen temperatures, while oxygen has a vapour pressure of 10^{4} Pa at liquid nitrogen temperatures [18]. In the high-vacuum TEM chamber, hydrogen and oxygen cannot be removed from the background gas while the water vapour pressure should be drastically reduced at the low temperatures achievable by the cold finger.

The cold finger was then cooled with liquid nitrogen and a new attempt was made to image another region of the SWNT sample. The SWNTs were now stable even at high magnification with a focused beam and high-beam current. Fig. 3c, d shows a small nanotube bundle extending from the sample being almost unaffected by 14 min of imaging. The nanotube bundle did not appear to be reduced in diameter or density, but rather seemed to deform slightly, as expected since knock-on collisions will create disorder in the structure.

The observed damage to the SWNTs when using a cold finger could be caused by electron irradiation-induced disordering in the nanotube structure [4]. The very limited damage rate when using the cold finger indicates that the actual beam current density in the TEM is likely to be considerably lower than our estimated maximal beam current density, $j_{\max}$. The above observations seem to support the hypothesis that water is the primary cause for the etching of the nanotubes from the outer shell. By using a cold finger at liquid nitrogen temperatures, the water can be removed from the background gas so that imaging of nanotubes can be done for tens of minutes with nearly no damage to the nanotube structure. If indeed water is such

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an important factor for the observed irradiation damage, it is possible that previous results on knock-on collisions should be carefully evaluated to check if such effects could influence the results.

3. Damage observed during SEM

The ionisation and dissociation cross sections for gas molecules are generally larger at low energies, i.e. in the 1–100 eV range [19], indicating that secondary electrons might be the main cause of irradiation-induced etching. If secondary electrons are the main initiators of the etching process, SEM imaging of carbon nanotubes could also have an influence on the nanotube structure despite the beam energy being well below the mentioned threshold for TEM irradiation damage. The image sequence in Fig. 4 shows a small MWNT first imaged in TEM, which was then transferred to a LEO 1550 SEM where a part of it was exposed for 4 min at 5 keV and then finally returned to the TEM to observe the effect of the SEM exposure. In the initial TEM image, the small MWNT had what appeared to be well-graphitised shells. The SEM image shows a small region of interest (ROI) with area of 0.05 μm^2 that was positioned such that only the lower part of the nanotube was exposed to the scanning beam. The electron beam current is known to be about 200 pA from previous measurements. The accumulated dose during a 4 min exposure in the ROI is hence of the order 1 $\mu C/\mu m^2$. The nanotube was then imaged in TEM again and Fig. 4c shows that the exposed lower part of the nanotube has been severely damaged by the SEM irradiation, while the upper unexposed part is relatively unaffected. As expected, continuous exposure in the TEM further damaged the nanotube as shown in Fig. 4d. We have observed both electron beam-induced deposition and etching of nanostructures in the SEM, depending on sample cleaning and both the sample and SEM history.

In the first image, the nanotube has a diameter of about 22 nm and after the SEM exposure the diameter has been reduced to at least 17 nm, corresponding to the loss of about 7 shells. The observed etch rate is, in this case, of the order 10 shells per $\mu C/\mu m^2$ (or 0.1 shell per C/cm^2).

4. Discussion

The observed etch rate imposes strict limits on the allowable exposure for carbon nanotubes devices if defect-free nanotubes are required. Since devices with highly sensitive nanotube components are often made by electron beam lithography (EBL), it is interesting that the required dose for exposing the resist is normally [20] of the order 10 $\mu C/cm^2$. The EBL exposure itself is hence orders of magnitude too low to remove an entire shell from a carbon nanotube, but would give rise to a damage probability of removing about 1 per 10^6 atoms for a SWNT. A (10,10) SWNT has 2×10^5 atoms/μm and for such a tube the EBL exposure alone could cause a defect for every 5 μm nanotube length. For EBL devices, the nanotubes are usually located by SEM to prepare the EBL pattern, before resist is spun onto the sample. Such SEM imaging will expose the nanotubes to a higher irradiation dose.

SEMs with oil diffusion pumped vacuum systems are in our experience particularly prone to deposition of carbonaceous material, while turbo pumped SEM systems generally show absolutely minimal deposition on clean samples. The diffusion pumped SEMs often have load lock systems attached while the turbo pumped system often opens the specimen chamber itself, exposing the interior to ambient air with water vapour when loading a sample. If EBL devices are made in a SEM with a carbonaceous background gas, the etch rates might be lower and the deposition effect will probably be seen to dominate.

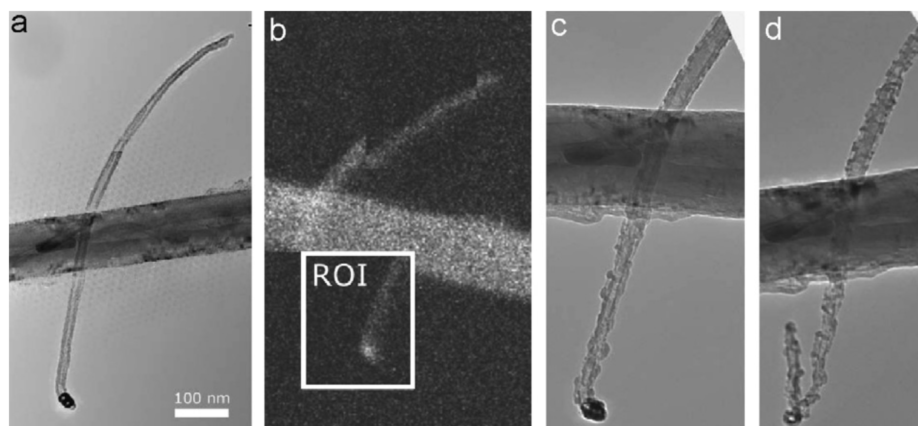

Fig. 4. SEM-induced etch of a MWNT. (a) TEM image of a small ∅ 22 nm MWNT adhering to a large MWNT suspended between two cantilevers. (b) SEM image showing how the lower part of the small MWNT was exposed to a 5 keV SEM beam for 4 min by selecting a small region of interest (ROI) in the SEM. (c) TEM image after the SEM exposure shows considerable damage to the exposed part of the tube. (d) Imaging in TEM without cold finger cooling also damaged the tube.

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5. Conclusion

The effects of TEM irradiation on MWNTs and SWNTs were studied. It was found that water vapour is likely to cause etching of the outer layers of carbon structures under electron irradiation, even with beam energies that were otherwise expected to be harmless to MWNTs. In the TEM system, the etching rate could be reduced to an almost negligible level by cooling a cold finger with liquid nitrogen. Just as the TEM irradiation, irradiation during SEM imaging of a MWNT was found to create pits in the shell structure, indicating that care must be taken when imaging and fabricating nanostructures in both SEM and TEM. Further studies of these effects in a wider range of electron microscopes and especially environmental electron microscopes would be valuable to investigate the chemical reactions taking place in more detail.

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