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In Situ Field Emission of Carbon Nanotubes in Oxygen Using Environmental TEM and the Influence of the Imaging Electron Beam

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One of the major applications of carbon nanotubes (CNTs) is as field emission electron sources in X-ray tubes for early cancer detection [1, 2]. The emission currents and lifetimes of CNTs are highly dependent on vacuum conditions, and are most optimized in ultrahigh vacuum (10^{-7} mbar or better). Under less stringent environments, CNTs are found to exhibit lower emission currents and reduced lifetimes [3, 4].

In this paper, we report the direct study on the structural changes in CNTs as they are heated and oxidized *in situ*, using aberration-corrected environmental TEM [5]. We established a protocol whereby heating and oxidation were performed without an imaging beam, and changes on identifiable nanotubes were documented after purging the gas from the chamber, to ensure that they were due to the effect of gaseous oxygen molecules on the nanotubes rather than the ionized gas species [5]. Our findings show that only the outside graphene layer is being removed and, on occasion, the interior inner wall is oxidized, presumably due to oxygen infiltrating into the hollow nanotube through an open end in the tube [5]. Contrary to earlier reports, preferential oxidation of CNT caps was not observed [5, 6].

In ETEM experiments, interaction between the incident electron beam and gas leads to ionization of gas molecules and increased reactivity. It is therefore important to understand the influence of the imaging electron beam and establish means to eliminate beam-induced artifacts. By maintaining beam illumination in the presence of O_2 gas, we find that there is a threshold cumulative electron dose which brings about visible damage in CNTs in oxygen – through removal of their graphitic walls and attack on their caps – which is dependent on O_2 pressure [7, 8]. Damage is less at lower pressures, decreasing by as much as five-fold per decade at low pressure [7]. There is no apparent lower limit to the electron dose rate at which nanotubes will not be destroyed [7]. Therefore, the best way to mitigate the influence of the imaging beam is to operate at cumulative dose not exceeding the threshold for a given O_2 pressure, through interplay of beam illumination and accumulated exposure time. This strategy has been successfully applied to observe the *in situ* field emission behaviour of CNTs in O_2 [8, 9], for their practical application as field emission sources. These results also provide guidelines on how to improve the lifetime of field-emitting CNTs, with better vacuum conditions.

References:
[1]. G. Cao et al., Med. Phys. 37 (2010), pp. 5306–5312.
[2] X. Qian et al., Med. Phys. 39 (2012), pp. 2090–2099.
[3] K. A. Dean and B. R. Chalamala, Appl. Phys. Lett. 75 (1999), pp. 3017–3019.
[4] J.-M. Bonard, et al., Ultramicroscopy 73 (1998), pp. 7–15.

[5] A. L. Koh et al., ACS Nano 7(3) (2013), pp. 2566–2572.
[6] R. Sinclair et al., Advanced Engineering Materials 16(5) (2014), pp. 476-481.
[7] A. L. Koh and R. Sinclair, Ultramicroscopy (2017), *in-press*. DOI: 10.1016/j.ultramic.2016.12.009
[8] A. L. Koh et al., Nano Lett. 16(2) (2016), pp. 856-863.
[9] A. L. Koh et al., Nanoscale 8 (2016), pp. 16405 – 16415.
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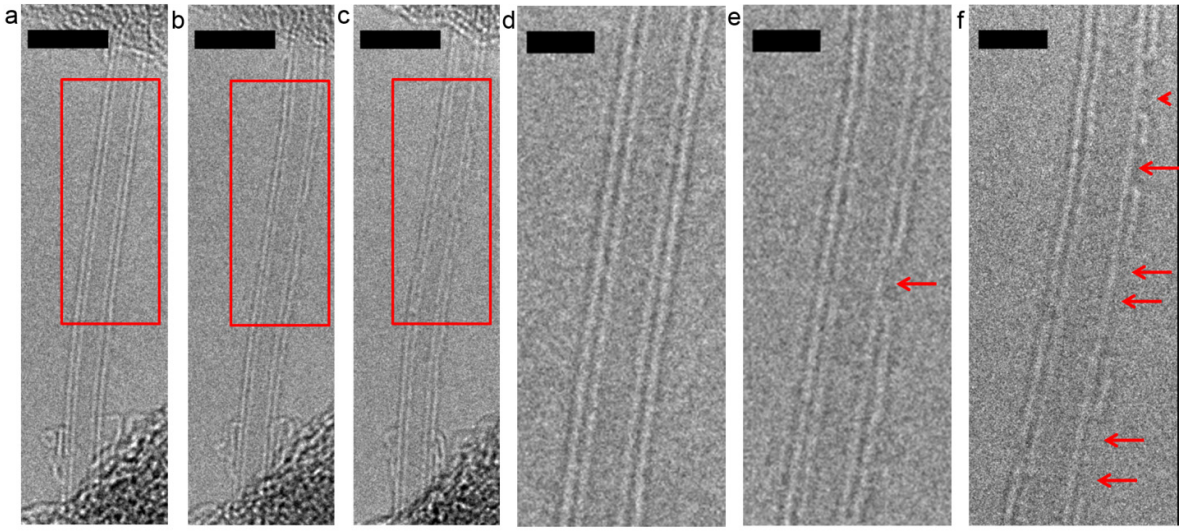

Figure 1. Aberration-corrected TEM images showing structural changes in a double-walled carbon nanotube at (a) 300°C before oxidation, (b) 300°C after 15 min exposure to 1.5 mbar oxygen, and (c) 400°C after 15 min exposure to 1.5 mbar oxygen. (d)- (f) are higher magnification TEM images of insets (a)-(c) indicated by the red boxes. Scale bars in (a)-(c) and (d)-(f) are 5 and 2 nm respectively. [5]

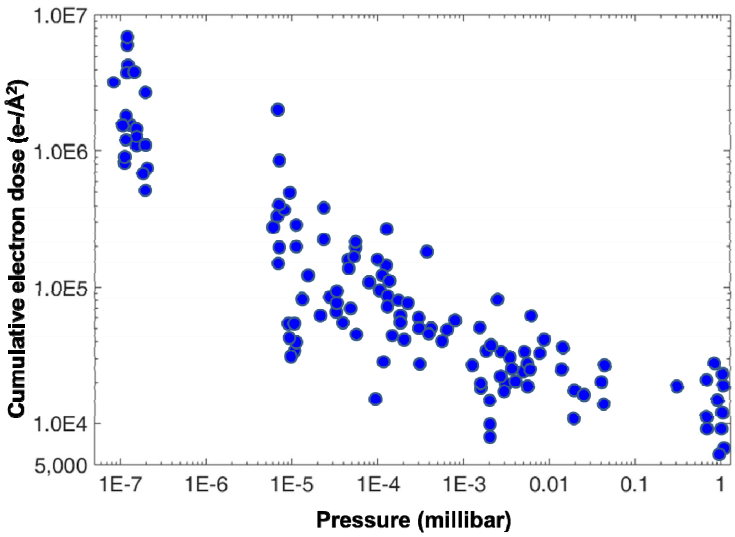

Figure 2. Cumulative electron dose (logarithmic scale) to damage carbon nanotubes by continuous 80 kV electron beam illumination as a function of O_2 pressure at room temperature. [7]