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Oxidation Studies of Carbon Nanotubes for Applications as X-Ray Field Emitters Using an Aberration-Corrected, Environmental TEM

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Since their discovery in 1991 carbon nanotubes (CNTs) [1] have found an increasing number of applications, most notably as field emission electron sources in X-ray tubes for medical applications [2, 3]. In a laboratory setting, field emission measurements of CNTs are usually carried out in an ultrahigh-vacuum system with base pressure of ~ 10^{-7} mbar or better. Under less stringent vacuum conditions, CNTs are found to exhibit lower emission currents and reduced lifetimes [4, 5]. Shortly after the discovery of CNTs, several groups attempted to utilize the oxidation process to manipulate their structures, for instance by opening up their terminating cap or by thinning the tubes [6, 7]. In the literature, these oxidation steps were usually performed in an external laboratory setting, and the state of the oxidized samples was surveyed *a posteriori* with a transmission electron microscope (TEM). However, because of their nanoscale, no direct study has been performed on the underlying mechanism of their oxidation.

In this paper, we report the direct study on the structural changes in CNTs as we oxidize them *in-situ* using an aberration-corrected environmental TEM (ETEM). The samples were first heated to 300°C in high-vacuum and a few nanotubes were identified for tracking. Then, with the electron beam blanked, 1.5 mbar of research grade (99.9999% purity) oxygen was introduced into the ETEM for 15 min while maintaining the temperature at 300°C. At the end of this cycle, the gas was purged from the ETEM while the temperature was kept at 300°C, and the same nanotubes were imaged to identify any differences after having been exposed to oxygen. The temperature was then increased to 400°C, the oxidation process was repeated, and the same set of nanotubes was tracked and imaged at 400 °C after oxygen was purged from the system. These oxidation procedures were repeated on samples mounted on different TEM grids with start and end temperatures of 400°C and 520°C, respectively

One important consideration during the oxidation experiment is the possible ionization of the gaseous species by the imaging electron beam. Therefore, in order to investigate the effect of gaseous oxygen molecules on the nanotubes, rather than ionized gas species, we established a protocol whereby heating and oxidation were performed without an imaging beam, and the changes on identifiable nanotubes were documented after purging the gas from the chamber. The imaging experiments were carried out at 80kV, below the knock-on displacement energy for single-walled carbon nanotubes [8].

Our studies show that the oxidation of multiwall CNTs proceeds layer by layer, starting with the outermost wall, and not initiating at the nanotube cap, as reported previously. Nanotubes with a larger

number of walls (greater than six) are found to be more resistant to oxidation, with all walls remaining intact during the ETEM experiments [9].

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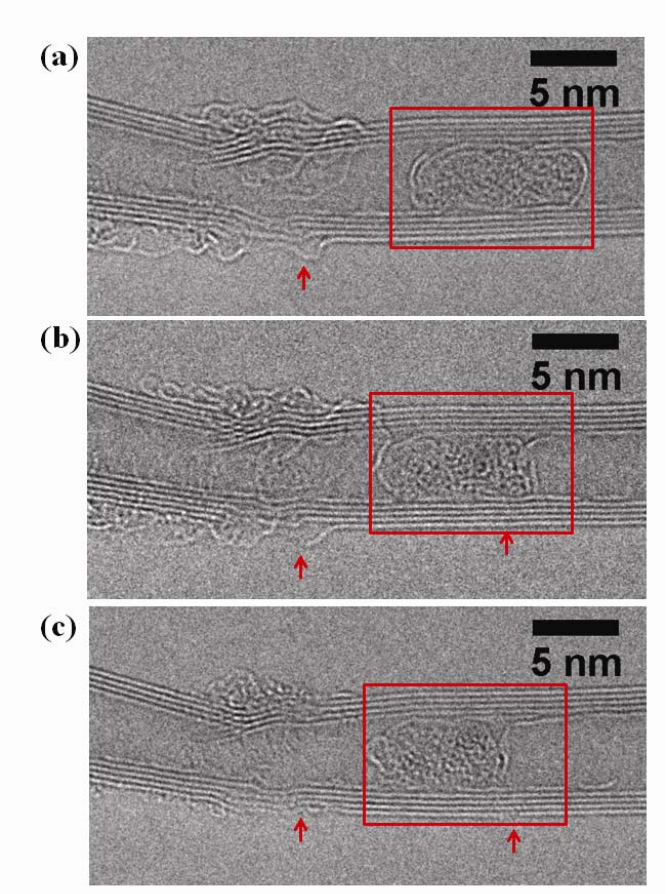

Figure 1. Aberration-corrected TEM images of the same CNT at (a) 400°C, (b) 400°C after exposure to 1.5 mbar oxygen and (c) 520°C after exposure to 1.5 mbar oxygen. Parts of the outer wall of the nanotube are removed as a result of exposure to oxygen, as indicated by the red arrows. Oxidation also occurs in the inner wall of the tube, evident from the reduction in the amorphous carbon area indicated by the red box.

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