Ultramicroscopy (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

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

Ai Leen Koh[a,*], Robert Sinclair[b]

[a] Stanford Nano Shared Facilities, Stanford University, Stanford, CA 94305, USA
[b] Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

ARTICLE INFO

Keywords:
Environmental transmission electron microsccopy
Oxidation
Electron dose
Carbon nanotubes
Beam damage

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 O_2 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 10^{0} 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 10^{0} mbar pressure regimes, and discusses the role of electron dose rate and total electron dose on beam-induced CNT degradation experiments.

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 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 O_2 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 O_2 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 (N_2) was used in place of O_2 [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 ~10^{0} mbar O_2 [22]. In the present work, we examine the effect of the electron beam on carbon nanotube oxidation behavior using lower O_2 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

* Corresponding author.
E-mail address: alkoh@stanford.edu (A.L. Koh).

http://dx.doi.org/10.1016/j.ultramic.2016.12.009
Received 1 August 2016; Received in revised form 23 November 2016; Accepted 6 December 2016

10^{-7} mbar to 10^{0} mbar O_2 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 O_2 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 O_2 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 O_2 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 (e–/Å^2 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 ~10^{-7} mbar to 10^{-1} mbar, and at varying electron dose rates of ~60 e–/Å^2 s to 4000 e–/Å^2 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 A/cm^2≡620 e–/Å^2 s.

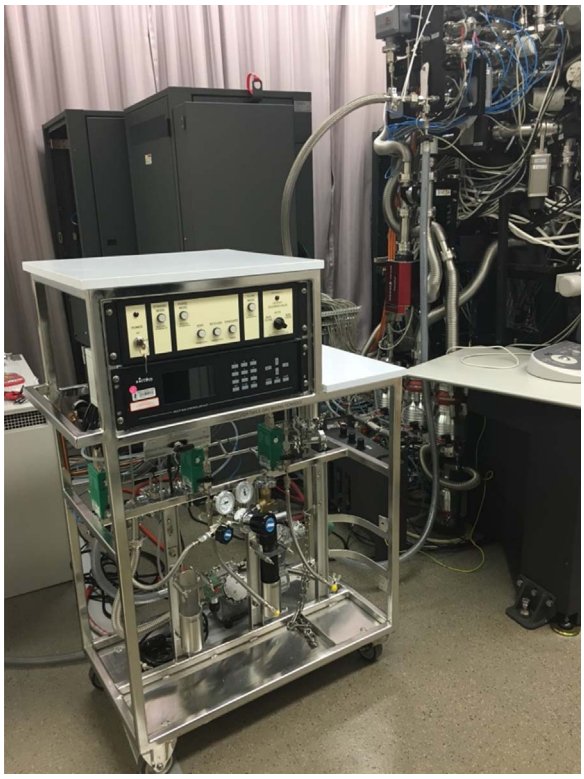

Fig. 1. Photograph of the gas mixing console beside the ETEM.

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 15 min 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 15 min each time, with the column valves closed during oxygen