Supporting Material for

Reinforcing Multi-Wall Carbon Nanotubes by Electron Beam Irradiation

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Sample preparation

Carbon Nanotubes (CNTs) were grown by Chemical Vapor Deposition. The first set of CNTs was produced by acetylene decomposition over Fe_2Co nanoparticles supported by $CaCO_3$ at 650°C growth temperature. The second set of CNTs was produced by ethylene decomposition over Fe nanoparticles supported by Al_2O_3. The growth was performed at 750°C in the presence of hydrogen and traces of water.

To prepare the samples for Transmission Electron Microscopy (TEM) imaging and Atomic Force Microscopy (AFM) measurements, as-grown carbon nanotubes were dispersed in isopropanol and sonicated using HD2200 homogenizer with a power of 20W for 5 minutes. To characterize the nanotubes by HRTEM, a droplet of the suspension was put on a Cu TEM grid with a lacey C film. Alternatively, we deposited a droplet of the suspension by dielectrophoresis on a Si_3N_4 membrane with pre-drilled 200 nm to 1 µm wide holes, prepared using photo- and electron beam- lithography processes. The substrate being compatible for both TEM and AFM, the measurements of the bending modulus have been performed on the same CNTs at each irradiation stage.

Instrumental

High Resolution Transmission Electron Microscopy (HRTEM) characterization was carried out using a Philips CM200 FEG microscope operating at 200 kV. TEM micrographs were taken with a Gatan Image Filter Tridiem with 2048x2048 pixels CCD detector. A sequence of images was recorded with the fast search mode (512x512 pixels) of the Digital Micrograph using the exposure time of 0.25 seconds and the frame rate of 4 frames/sec. High-resolution images were taken about every minute with an exposure time of two seconds by binning the pixels twice (1024x1024 pixel) in order to increase the contrast without increasing the exposure time. The flux calibration was performed using one image (1 second exposure time) taken without the sample in the beam. The flux was calculated by taking the ratio of the added number of electrons on the CCD camera and the area.

Scanning Transmission Electron Microscopy (STEM) irradiation was carried out using a Philips CM20 microscope operating at 200 kV. Scan rate was of 2.5 milliseconds per line for 288 lines per frame. The flux calibration was performed by measuring the current thought the fluorescent screen without the sample in the beam. The flux was calculated by taking the ratio of the measured current and the scanned area. The electron flux was about 10^{17} e/cm²s and was measured before and after irradiation.

AFM force measurement was carried out by using the "swiss cheese" method. The CNTs, suspended over a hole in a Si_3N_4 membrane, were deflected using an AFM tip. The deflection was recorded as 3D images. Knowing the applied force, the deflection and the geometrical parameters of the CNT, we could extract the bending modulus using Eq. (1).

Table 1
Measured mechanical properties for both irradiated carbon nanotubes.

Sample no.	Outer diameter d (nm)	Irradiation dose (e/cm^2)	Bending modulus E_b, as-grown (GPa)	Bending modulus E_b, after irradiation (GPa)
1	30	$1.38x10^{19}$	3.48	2
2	20	$1.48x10^{19}$	17.99	215.57
3	16	$3.01x10^{19}$	120	690
4	12	$1.11x10^{19}$	461	1202
5	50	$1.64x10^{19}$	13	6
6	16	$2.19x10^{19}$	444	832
7	16	$2.19x10^{19}$	237	145
8	25	$2.57x10^{19}$	78.7	74.1
9	16	$2.57x10^{19}$	56.3	245
10	11	$3.86x10^{19}$	696	1230

Movies

5 movies are presented in association with the manuscript at the project home page http://lnnme.epfl.ch/page85890.html:

Movie 1 *(file TEM-reconstruction-dynamics.mov)*: Time evolution of the HRTEM image during sample exposure to the electron beam in the microscope. The movie represents a sequence of images recorded with the fast search mode (512x512 pixels) of the Digital Micrograph using exposure time of 0.25 seconds and frame rate of 4 frames/sec.

Movie 2 *(file crosslink-zigzag-AA.mpg)*: Visualization of the molecular dynamics simulation of cross-link formation in an AA-stacked graphene bi-layer strip with a zigzag edge. The plane and the edges of the graphene bi-layer strip are normal to the viewing plane.

Movie 3 *(file crosslink-zigzag-AB.mpg)*: Visualization of the molecular dynamics simulation of cross-link formation in an AB-stacked graphene bi-layer strip with a zigzag edge. The plane and the edges of the graphene bi-layer strip are normal to the viewing plane.

Movie 4 *(file crosslink-armchair-AA.mpg)*: Visualization of the molecular dynamics simulation of cross-link formation in an AA-stacked graphene bi-layer strip with an armchair edge. The plane and the edges of the graphene bi-layer strip are normal to the viewing plane.

Movie 5 *(file crosslink-armchair-AB.mov)*: Visualization of the molecular dynamics simulation of cross-link formation in an AB-stacked graphene bi-layer strip with an armchair edge. The plane and the edges of the graphene bi-layer strip are normal to the viewing plane.