Quantitative High-Resolution TEM/STEM and Diffraction

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Electron irradiation damage in dependence of the acceleration voltage studied by C_C/C_S corrected HRTEM on the example of functionalized carbon nanotubes

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Aberration corrected high resolution transmission electron microscopy (AC-HRTEM) at conventional accelerating voltages of 200 or 300 kV allows atomic structural investigations at sub-Ångstrøm point resolution. Samples made of light atoms like carbon nanostructures or Li-based materials are easily subjected to knock-on damage at 200 keV and higher energies. The nowadays state-of-the-art is to operate the C_S-corrected microscopes at 80 kV to lower the damage of carbon nanostructures like graphene and carbon nanotubes. But even 80 keV energies are sufficient to damage delicate objected like C_{60} molecules and other organic molecules that are supported by free-standing graphene sheets of filled into nanotubes (nanotubes and graphene act as sample/object holder). Operating a TEM considerably below 80 kV e.g. 40 kV or less requires the correction not only of the spherical aberration but also of higher order geometric aberrations up to the 5^{th} order. Moreover, the correction of chromatic aberrations is necessary to archive atomic resolution at high contrast [1].

We are going to study by TEM single-walled and double-walled carbon nanotubes that are filled and functionalized with molecules like C_{60}, tetrathiafulvalene (TTF, sulphur rich molecule) [2] or metal carbonyls [3]. The effect of the electron beam on the behaviour of nanotubes and their fillings is investigated as function of electron energy (80, 40, 20 keV), total electron dose, and electron dose rate. A dedicated aberration corrector is used to archive atomic resolution at lower voltages especially at 20 and 40 kV. Geometric axial aberrations are corrected up to the 5^{th} order except for C_5 that was designed to be 4 mm to obtain an optimized phase contrast transfer function. Off-axial aberrations are corrected up to the 2^{nd} order for larger fields of view as well as chromatic aberrations for increased contrast.

Figure 1 shows as example HRTEM images of C_{60} molecules at different stages of electron irradiation. At 80 kV already a relatively small accumulated dose of $5x10^{-7}$ e^-/nm^2 is sufficient to form first dimers of C_{60} (this dose corresponds to just about 4 or 5 HRTEM acquisitions at conventional dose rates in the order of some 10^6 $e^-/nm^2/s$). However, no visible changes of the structure of C_{60} molecules are visible at 40 kV after irradiation with the same accumulated electron dose. A coalescence of the C_{60} molecules is clearly visible at a electron dose of $2x10^{-8}$ e^-/nm^2 and 80 kV irradiation. It requires almost two magnitudes of order higher dose (40 times) to get small hints of coalescence of the C_{60} molecules at 40 kV. Unfortunately, at 40 kV increased dynamics such as the typical vibrations of free-standing carbon nanotubes and longitudinal motion of C_{60} molecules lowered the image contrast and resolution. Part of the reduced contrast at 40kV might also arise from an image spread within the corrector. An image spread is almost equivalent to a Debye-Waller factor and hence cannot be distinguished from vibrations of the tube.

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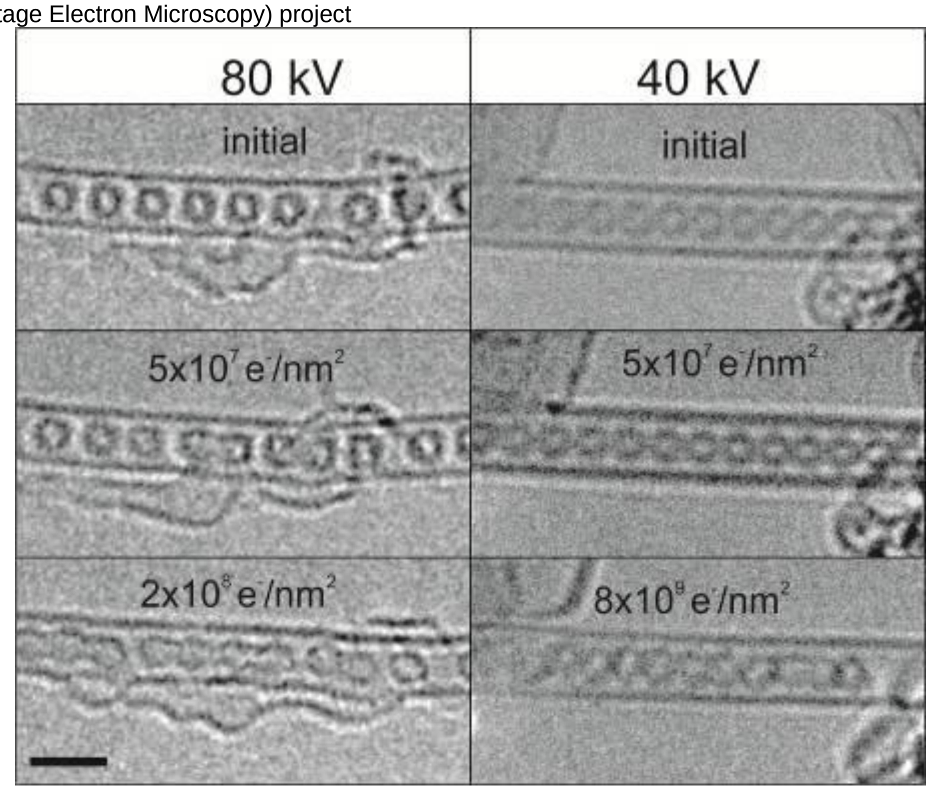

Figure 1. Aberration corrected HRTEM images of C_{60} molecules in carbon nanotubes. (left) C_{60} in a double-walled carbon nanotube imaged at 80 kV. (right) C_{60} in a single-walled carbon nanotube imaged at 40 kV. Dimers (two connected C_{60} molecules) occurs at a dose ca. $5x10^{-7}$ e^{-}/nm^{2} at 80 kV at 40 kV no changes are visible. A coalescence of the C_{60} molecules is clearly visible at a dose of $2x10^{-8}$ e^{-}/nm^{2} and 80 kV irradiation. At 40kV it requires almost two times magnitude of order higher dose (40 times) to get first indications of coalescence and rupturing of the C_{60} molecules. (size of scalebar is 1 nm).