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Imaging and Spectroscopy of Carbon Nanostructures with 80 and 20 keV Electrons

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Graphene, an atomic mono-layer of hexagonally ordered carbon atoms, is an outstanding new material of fundamental scientific and practical importance. The remarkable physical properties of this material depend directly on the atomic defect structure. Moreover, under special circumstances it begets other carbon nanostructures; fullerenes [1], carbon chains [2] and carbon nanotubes (CNT). The understanding of transformation routes between carbon nanostructures, the knowledge why particular defect configurations have been formed, their dynamics and properties is the key for further understanding and control of chemical and physical functionality, and hence their practical applications. Here graphene is used as a substrate and CNTs as transparent nano-testtube for complex molecules. The imaging of such molecules with atomic resolution is our ultimate goal. The path-goal line is to understand radiation damage effects resulting from the interaction of beam electrons with the atoms of the object at electron energies below the knock-on threshold for carbon atoms in graphene and CNTs., The data will be obtained from C_S-corrected high-resolution transmission electron microscopy (AC-HRTEM) and electron energy loss spectroscopy (EELS). First. results are presented for electron beam energies of 80 and 20 keV using the commercial FEI-*TITAN*80-300 (at 80 keV) and the prototype Zeiss-*SALVE* (Libra-based) microscopes (predominately at 20 keV). The latter instrument is equipped with a monochromator which enables imaging with high contrast at high spatial frequencies as well as spectroscopy with exceptionally low background noise in the low loss region near the zero loss peak [3].

At present the *SALVE* prototype microscope has the following properties: (a) the monochromator slit width of 2 μm provides a FWHM of 0.15eV for the incident electron beam, (b) the OMEGA filter is always turned on. EELS is carried out using a smaller slit of the monochromator of 1 μm resulting in an energy FWHM <0.1 eV. Images and spectra are recorded by either a Gatan Ultrascan 1000 2k × 2k CCD camera or by a TVIPS T416 4k × 4k CMOS camera. The information limit of the microscope at 20 kV is determined by the combination of image spread and focus spread [4]. The focus spread limit can be reduced from 0.5 nm without monochromator to 0.25 nm with monochromator. The image spread limit, which includes all kinds of lateral noise, has been determined to be better than 0.18 nm.

Calculations of the contrast of energy- filtered images of graphene at 80 keV and 20 keV show that at the lower electron energy the contribution of the non-linear terms to the image contrast cannot be neglected. The experimental zero-loss filtered HRTEM [3] images at 20 keV show largely increased contrast and a transfer of the 213 pm reflection in the case of tilted illumination. We deduce a quasi-linear dispersion of graphene from momentum resolved EELS experiments at 20 keV [5]. Further results will be shown on functionalisation and imaging of modified graphene by: (1) a local electron-beam induced amorphization with 300 keV electrons but imaging with 80 keV electrons [6], (2) N substitution in graphene by N-implantion of CVD grown graphene. We shall demonstrate that charge redistribution around nitrogen substitutions of single carbon atoms due to chemical bonding effects is visible in an AC-HRTEM image [7]. First results on image contrast of DNA as well as imaging and spectroscopy on semiconductor quantum dots passivated with polymer on a graphene substrates will be presented.

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In adddition we shall present results of the interaction of the electron beam with functionalized CNTs. At 80 keV, AC-HRTEM provides structural information on both, the exterior (functional groups) and/or the interior of individual fullerenes, metallofullerenes [8,9] or metal clusters at the near-atomic level in direct space and real time. However, using the examples of C_{60} fullerenes, metal atoms and endohedral $M_3N@C_{80}$ functionalised with an organic group imaged, respectively, in SWNT, we demonstrate that radiation damage at 80 keV still breaks fullerenes and functional groups preventing their atomic resolution [9]. Moreover, our investigations clearly show the importance of lowering the electron energy for the stability of fullerene molecules inside CNTs, as we measure that they accept an about 100 times higher electron dose at 20 keV than at 80 keV [4]. Future prospects of sub-Angstrom low-voltage electron (SALVE) microscopy with C_C and C_S correction and of energy filtered TEM with sub eV energy selecting windows will be reported as well.

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