ESRF	**Experiment title:** EXAFS Structural Study of Metal Halide Nanowires in Single-walled Carbon Nanotubes	**Experiment number**: CH-1598
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Single walled carbon nanotubes (SWNTs) are emerging as ideal model systems for studying discrete and atomically regulated crystal growth [1]. Open SWNTs, composed of rolled sheets of sp^2 graphene carbon terminated at one end by fullerenic carbon hemispheres, form well-defined cylindrical cavities within a strictly limited diameter range (typically 1-2 nm). The internal van der Waals surfaces of SWNTs regulate the growth of encapsulated materials in a very precise fashion. Crystal growth within SWNTs is atomically regulated, and nanoscale crystals with precise integral layer architectures ("Feynman crystals") can be formed.

In Oxford we have successfully established a general method of filling open SWNTs with ionic binary metal halides by capillary wetting. Molten halide salts are introduced into the SWNTs by direct wetting at high temperature under vacuum [1]. Confinement of the halides within the SWNT capillaries produces reduced or modified coordination structures. The guest materials are restricted to as few as 2-3 atomic layers in cross-section, forming structures in which entire layers of coordinating ions have been excluded. In some cases, entirely novel coordinations and stereochemistry are observed. For example, KI nanowires within 1.4 nm diameter SWNTs [2] are restricted to a lattice structure of 2×2 ions in cross-section. All K^+ and I^- ions are on the surface and are reduced in coordination from 6:6 to 4:4.

Our ESRF experiment aimed to use EXAFS to obtain structural information on metal halide nanowires encapsulated within SWNTs. The 1-D nature of these nanowires makes them extremely interesting objects to study, as quantum confinement effects have important consequences at this scale. One must however obtain detailed structural information to be able to predict and interpret potential new properties. EXAFS is an ideal tool to characterise in detail these nano-structures and compare them to their bulk. While High-Resolution Transmission Electron Microscopy with image reconstruction software [1-3] enables atomic resolution images of individual nanowires to be obtained, EXAFS provides an element-specific measure of the average coordination environment of the atoms throughout the samples. This complementary information enables us to refine synthesis parameters and is a crucial step toward using these new materials in technological applications.

The single-walled carbon nanotubes were produced by arc discharge, opened with HCl, and filled with metal halides using the capillary wetting technique. Special care was taken to remove any extraneous material (i.e metal halide not inside the nanotubes) to ensure only the filling would contribute to the measured signal. We were able to acquire data on the following systems: CsI@SWNT, FeI_2@SWNT, NiI_2@SWNT, and LaI_3@SWNT. These were chosen as they have already been studied by HRTEM and have interesting potential properties. Bulk metal halides were used as structural and oxidation state standards. Both bulk and nanowire@SWNT samples were mixed with boron nitride and pressed to produce 13 mm pellets. For each sample, EXAFS data were obtained at the metal K-edges and the iodine K-edge, for structural characterisation of the coordination environment of the metal cations and iodide anions.

ESRF beamline BM29 was the ideal location to perform this experiment, as the Si(311) monochromator gave access to the full energy range (7 – 40 keV) required, and both transmission and fluorescence are readily available. We initially collected data from the nanowires in fluorescence mode, but some sample quantities and filling yields proved sufficient to acquire spectra in transmission. Data were collected to k = 16 $Å^{-1}$. Multiple datasets were acquired overnight in order to improve the signal-to-noise ratio. All the samples were studied under cryogenic conditions to reduce thermal vibration as much as possible.

Analysis of the results is in progress with the Daresbury laboratory software suite (Exback, Excurv98). Both the XANES and the EXAFS signals show significant differences between the nanowire@SWNT samples and the bulk metal halides. This indicates that the average nanowire crystal structures differ significantly from the bulk lattices. In the CsI nanowires, the rocksalt 6:6 structure is suggested instead of the 8:8 structure of bulk CsI. However, for this sample, EXAFS oscillations were obtained only to low k-values, implying that the CsI nanowires lack structural order even at short range. Other nanowires such as FeI_2 gave clear EXAFS oscillation to higher k-values. Work is now underway to fit all the data with structural models built from High Resolution Electron Microscopy studies.

X-ray absorption at the nickel K-edge was also detected in some of our samples. This is an unexpected but highly significant observation. Nickel is used as a catalyst during the carbon nanotube synthesis, and it was believed that the purification procedures are sufficient to remove all remaining catalyst particles from the samples. However the Ni K-edge EXAFS shows the presence of residual nickel or nickel carbide. We also observed variation of the nickel XANES, which suggests the nickel might interact with the filling process on some occasions. As a result, improved purification processes for the nanotubes have now been developed, and are already in place.

We have recently extended the capillary wetting process to achieve the filling of SWNTs with metal chalcogenides. This kind of system, semiconducting materials within nanotubes, is extremely interesting as the band structure of the encapsulated semiconductor will be altered by a size effect (blue shift) and the 1-D geometry. In the final, additional part of our experiment, we were able to study a first sample of HgTe filled nanotubes at the Hg L_3-edge and the Te K-edge. The spectra showed clear differences from bulk HgTe both in the XANES and EXAFS. However, the S/N ratio in this preliminary study was too low to allow any detailed analysis. Having successfully proved the feasibility of using EXAFS to study metal chalcogenide nanowires, we plan a future experiment to study these materials using extended data acquisition times.

[1] J. Sloan, A. I. Kirkland, J. L. Hutchison & M. L. H. Green, *Chem. Commun.* 1319 (2002)

[2] J. Sloan et al., *Chem. Phys. Lett.* **329**, 61 (2000)

[3] R. R. Meyer, J. Sloan et al., *Science* **289**, 1324 (2000)