Extreme Nanowires: The Smallest Crystals in the Smallest Nanotubes

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A logical extension to fabrication of monolayer 2D materials such as graphene is creation of ‘Extreme Nanowires’ (i.e. Fig. 1), down to a single atom column in width.[1,2] In this limit, crystals have fundamentally different physical characteristics and properties.[3-5] We and others have created atomically regulated nanowires by confining them within the smallest diameter carbon nanotubes (i.e. either single walled carbon nanotubes (SWNTs) or double walled carbon nanotubes (DWNTs)), and are investigating their structural and electronic properties. These materials also provide an ultimate benchmark for testing the most sensitive characterisation methodologies which, when corroborated with suitable theory, will provide new data on physics at the most fundamental length scale accessible to nanomaterials fabrication. The most powerful investigative tools for structural investigation are aberration-corrected Transmission Electron Microscopy (ac-TEM) and Scanning Transmission Electron Microscopy (ac-STEM) and, here, we describe the application of these methods to a variety of Extreme Nanowire systems.

One of the most crucial aspects of the role of electron microscopy in our investigation is the 2D and 3D elucidation of the structure of quasi- or true 1D nanowires formed in SWNTs as these form the primary source of information for density functional theory (DFT) and other ab initio theoretical approaches to both structure and properties elucidation. When combined with real physical measurements, this combined approach becomes even more powerful as we can start to piece together how the fundamental physics of a crystalline nanowire changes once we constrain its width down to one or two atoms in cross section. For example we recently record Raman Spectra from 2x2 atom thick HgTe nanowires embedded within 1.2-1.4 nm SWNTs[4] and found that we are able to model the Raman-measured lattice phonons of this system based on a simple structural model previously determined from two pairs of Exit Wave Reconstruction images which we also used to make DFT predictions about the altered electronic structure of this system which is predicted to change from a -0.3 eV semi-metal to a ~1.2 eV band gap semiconductor.[3] Following on from the exciting recent work of Senga et al.[2] who imaged the first true 1D crystals of CsI in DWNTs we are now modeling single atomic chain coils of tellurium within narrow SWNTs (Fig. 2).[6]

References:
[6] To be published
Figure 1. a) Structure and symmetry of ‘Extreme Nanowires’ in SWNTs: (l to r) 1x1 CsI, 2x2 SnSe, distorted 2x2 HgTe; b) AC-TEM of discrete CsI chain in narrow SWNT; c) AC-TEM image of 2x2 SnSe in a SWNT; d) Raman Spectrum (top) of SWNT bundles filled with HgTe (laser energy 1.76 eV). (bottom) Crystal structure of distorted HgTe previously solved by HRTEM [3,4]; (right) Bg and Ag symmetry Phonon modes predicted from DFT.

Figure 2. a) Bulk crystal structure (unit cell) of pure tellurium with enlarged Te column spiral; b) Atomic chains of Te in SWNTs predicted by Ab-Initio Random Structure Searching (AIRSS); c) ‘zig-zag’ atomic chain of Te in a SWNT; d), e) and f) AC-TEM image, detail and situation and AIRSS Model (used in the simulation) of Te atomic coils observed in narrow SWNTs.