<u>Proposal for SuperSTEM time:</u> ADF and Spectroscopic Imaging of $CsSnI_3$-perovskite-like crystals in Single Walled Nano Tubes (SWNTs)

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Background and previous work

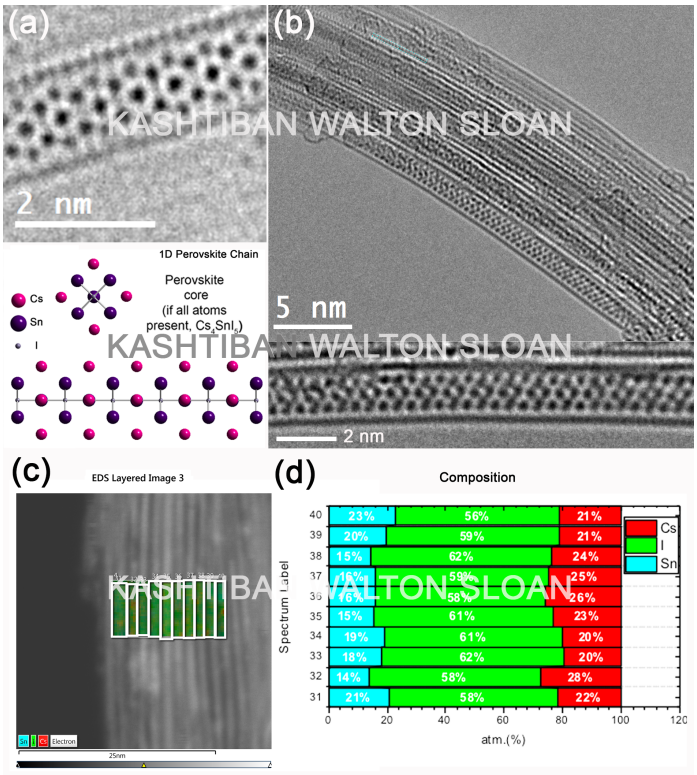

Fig. 1(a) Aberration corrected HRTEM image of nominally $CsSnI_3$ composition encapsulated in a ~1.38 nm diameter SWCNT although the inset model (bottom), which retains the perovskite structure, by inspection has a stoichiometry of Cs_4SnI_5 if full occupancy; (b) additionally aberration corrected HRTEM image of a SWNT bundle filled with $CsSnI_3$ with inset enlarged microstructure image; (c) ADF image of a $CsSnI_3$-filled SWCNT bundle with insets corresponding to individual EDX-mapped regions. (d) the average percentages of Cs, Sn and I in the mapped subregions in (c) are shown. Broadly speaking, the bulk $CsSnI_3$ stoichiometry is retained but some local fluctuations are evident indicating possible disproportionation during filling.

Nanowires formed by filling the central pore of single walled carbon nanotubes (SWCNTs) have extremely small diameters and can be constrained to as little as 1-3 atoms thick in cross section, equivalent to a single row of atoms or a partial unit cell or single unit cell of simple binary or ternary structures. Such encapsulation can enforce radical properties changes on the embedded materials resulting, for example, in the practical realisation of Peierls distortions for metallic 1D chains of tellurium [1] or dramatic enhancement of the Seebeck coefficient in the case of thermoelectric materials such as SnTe [2].

To date, however, nearly all of our recent work has focussed on single element or binary materials with very little effort expended on ternary systems apart from a $AgCl_{1-x}I_x$ solid solution with variable composition [3]. We have just had a new success incorporating the photovoltaic perovskite phase $CsSnI_3$ [4,5] into intermediate diameter SWCNTs and preliminary studies show that this material exhibits both a high degree of crystallinity (Figs. 1(a)-(b)) and compositional uniformity although there is some evidence of small local variations in this (Figs. 1(c)-(d)). Most excitingly, the embedded microstructures appear to retain key structural features from the parent $CsSnI_3$ perovskite making these materials the lowest dimension perovskite-like materials ever synthesised, potentially a highly prestigious result. For properties evaluation, this material has the added benefit of being in embedded carbon as the bulk phase is both air and moisture sensitive. We however need a much more accurate and comprehensive characterisation of these embedded crystal structures, especially in terms of the precise atom content of individual atomic motifs which will lead to a better understanding of the local fluctuation in stoichiometry (Fig. 1(d)). This will be necessary in order to circumvent potential ambiguity in crystallography interpretation and also a more complete and unambiguous interpretation of the true nature of the embedded crystal structures will be an important first step in *ab initio* properties evaluation and will further lead to the separation of particular perovskite-like structures into pure phases utilising ultracentrifuge protocols being developed in Warwick. We therefore require more quantitative Z-contrast STEM imaging and also atomic resolution EELS spectroscopic imaging in order to verify both local crystallography and composition with the highest possible precision.

Proposed experiment

In light of the above, we request 2 days 'Rapid Access' experiment time on SuperSTEM3 in order to perform the highest possible resolution HAADF imaging and EELS spectroscopic imaging with single atom sensitivity of these ternary phases. We specifically need precise compositional information on individual embedded crystals (e.g. such as in Figs. 1(a)-(b)) and also any evidence of compositional fluctuation possibly as a result of disproportionation (i.e. segregation of crystals with varying stoichiometry in different SWCNTs). Specimen grids will be provided by us but also fresh raw specimen in order to insure against possible sample contamination *in transit*. For possible correlation, for example with OptaDOS theory [1,2], we will also need high quality HREELS/ENLES spectra on this material which will indicate also any local variation in electronic structure as a function either of encapsulation or disproportionation. The band gap tunability as a result materials confinement within SWCNTs of varying diameter also provide important optical properties information. Employing the power of SuperSTEM3 in conducting VEEL mode will cover the bandgap studies into this exciting new material.

References

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