AR-TEM and STEM studies of Encapsulated PCMs in Narrow to Medium Diameter SWCNTs

Slade, C.[1]

[1] University of Warwick, United Kingdom

Encapsulated SnSe and Sb_2S_3 in medium to narrow single wall carbon nanotubes (SWCNTs) have been imaged and analysed using Atomic Resolution Transmission Electron Microscopy (AR-TEM) & Scanning Transmission Electron Microscopy (STEM) at 80kV. The discovery of a new form of confined SnSe offers another dimension in the investigation of this compound as a nano-Confined Phase Change Material (nC-PCM)[1] as opposed to other types of crystalline fillings.[2-4]

SWCNTs are thermally stable up to temperatures of 1400K, which makes them particularly suitable for investigations into the properties and structural transformation of nC-PCMs.[5] The van der Waals forces at the internal surfaces of the SWCNTs act to constrain the encapsulated material to surfaces with cross-sections down to $1nm^2$. This results in structures that can often vary wildly from that of the bulk form of the material. A bulk form of the respective PCM was Vapour Phase Transported (VPT) and deposited inside SWCNTs, with diameters in the range (0.7 - 1.7) nm, via the sublimation method. This method utilises a silica quartz double ampoule sealed under vacuum, with the filling material separated from the SWCNTs by a neck in the ampoule.

The previously reported 2x2 cubic structure of encapsulated SnSe in narrow SWCNTs has been observed (Fig. 1a), as well as a new, currently undefined, structure (Fig. 2). Phase contrast (TEM) studies have also shown the formation of more bulk-like rocksalt SnSe structures in the wider SWCNTs (Fig. 1b). This is as expected from previous findings and theory, which have also reported the existence of a distorted orthorhombic layered nC-SnSe structure. Presented here is a catalogue of models and images of the observed structures of nC-SnSe, and nC- Sb_2S_3.

Reported here is evidence of quantitative filling of SWCNTs with SnSe and Sb_2S_3, alongside structural modelling, and some examples of in- and ex-situ phase change behaviour with associated data. These results also form the basis for studies into further nC-PCMs, such as GeTe and PbTe. In particular, investigations into the variation of the structure of the encapsulated material as a function of the diameter of the NT, and the effect that this has on in-situ phase changes.

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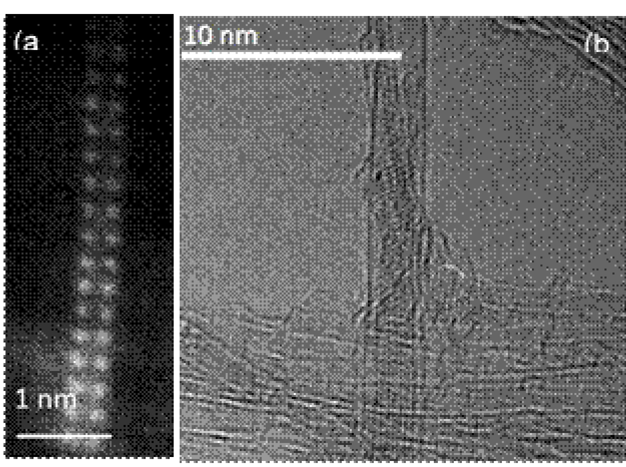

Fig. 1
(a) STEM image of the 2x2 cubic structure of nC-PCM SnSe in a SWCNT. The image has been Wiener filtered to uniformly reduce noise.
(b) AR-TEM image of nC-SnSe in a wide diameter and (superimposed) narrower diameter SWCNT. The thicker SWCNT encapsulates a bulk-like rocksalt form of SnSe, with the thinner, overlaying SWCNT confining a cubic structure.

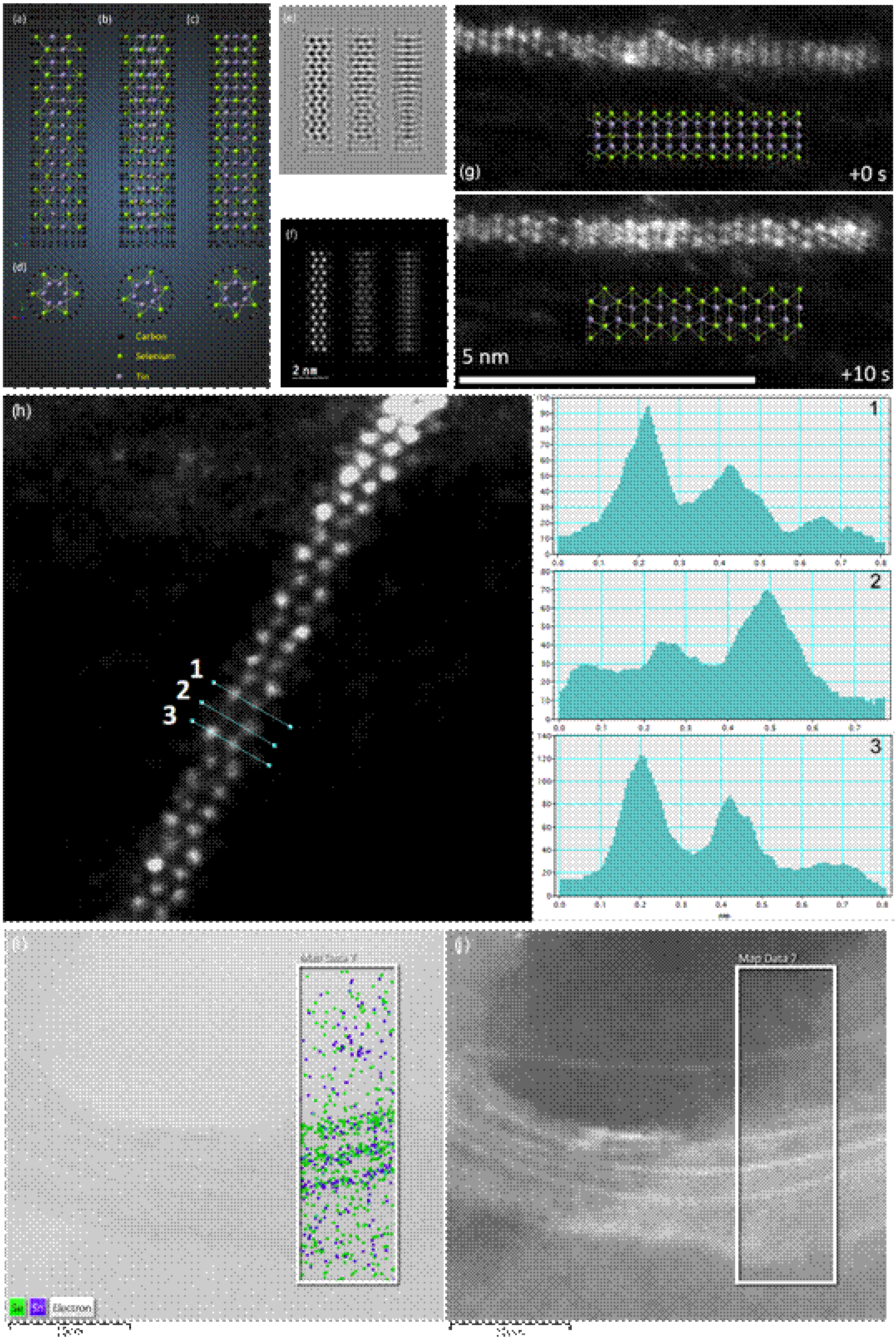

Fig. 2
STEM imaging, analysis and modelling of the new form of nC-SnSe, including EDS quantification of the composition of the encapsulated material.
(a)-(d) Models of the new form of nC-SnSe, with (b) and (c) being the model shown in (a) at rotations of 30° and 60°, respectively.
(f) and (g) are the corresponding TEM & STEM simulations, respectively.
(g) Two experimental STEM images, taken 10s apart, alongside the corresponding model view showing how the nC-SnSe rotates inside the SWCNT over time.
(h) An ELMA and gaussian-filtered STEM image of the new structure with corresponding line profiles. This filter method was used to uniformly reduce noise, without changing the relative intensities.
(i) EDS mapping of the composition of the encapsulated material over the indicated area, overlaying an ABF image.
The corresponding STEM image is shown in (j).