

Low dimensional crystallisation behaviour within single walled carbon nanotubes revealed by HRTEM

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Summary: The filling of single walled carbon nanotubes (SWNTs) with metal halides results in low dimensional crystallisation behaviour that is a function of both the structural complexity of the incorporated halide and the confining van der Waals surface of the incorporating tubules. Metal halides with simple packed 3D structures form similar structures within SWNTs while metal halides that form 3D-complex, layered or polyhedral chain structures form aligned 1D-polyhedral chain structures inside SWNTs. The HRTEM imaging properties of these composites are described.

1. Introduction

Single walled carbon nanotubes (SWNTs) provide a unique environment in which to study the low dimensional crystallisation behaviour of solid phase materials *via* HRTEM. Individually, SWNTs consist of sp^2 carbon cylinders with lengths in the μm range and diameters varying from *ca.* 1 nm up to *ca.* 4 nm, although the majority (80-90%) exist within a narrow 1.4-1.6nm range. SWNTs can be filled with a variety of metals and metal halides either by solution-deposition or capillary wetting (1-4) and this work has led to the observation of low dimensional crystal growth behaviour within their capillaries. As a wide variety of metal halides are available for filling SWNTs, it is possible to describe the crystallisation properties systematically as a function both of the bulk structural properties of the incorporated material and also in terms of their respective HRTEM imaging properties. The latter may be 'tailored' by varying compositionally the scattering power of the constituent cations and anions of a particular SWNT incorporated structure type.

2. HRTEM imaging of SWNT encapsulates

In Figure 1, we present some typical results of SWNT incorporated halides. Figs 1(a) and (b) show a HRTEM image and structural representation of CsCl formed within a SWNT. The lattice image shows a three atomic layer thick crystal aligned along a SWNT capillary. This structure is curious as it does not bear any obvious relation to the normal *bcc* structure of bulk CsCl. The structure appears to be closer to the rocksalt form (represented in Fig. 1(b)) and support for this interpretation is given by the observed 0.69 nm separation of the dark spots in the image, which corresponds to a_0 of the rocksalt form of CsCl. Another (less likely) possibility for this structure is a [110] section through the *bcc* CsCl structure-type lattice (not shown).

Fig 1(a). shows a lattice image obtained from a SWNT filled with a 1D crystal of ThCl_4 . The filling was obtained by intimate mixing of SWNTs with a $\text{KCl}:\text{ThCl}_4$ mix (corresponding to *ca.* KThCl_5), so the product may contain intercalated K^+ ions. In this structure, however, it is the incorporated Th^{4+} cations which dominate the image contrast and we can use the imaged lattice to predict the intercalated structure, as shown in Fig. 1(d). The idealised structure is based on a 1D chain of edge-linked ThCl_8 polyhedra, which corresponds to a section of the bulk structure. To complete the structural model, charge balancing (resulting in lower coordination for Th^{4+}) is necessary. In Fig. 1(e) We see another example of an incorporated ThCl_4 crystal, the growth progress of which is blocked by the presence of fullerenes [5]. The presence of fullerenes incorporated into SWNTs was previously shown by Smith et al. [6].

Fig. 1(b) shows an example of a 'twisted' crystal of CdCl_2 formed within a SWNT. In Fig. 1(g), we see the bulk layered structure of CdCl_2 and in Figs. 1(h) and (i), we see a structural representation and van der Waals surface showing how a section obtained from the bulk structure fits into a SWNT. The latter demonstrates that only a single CdCl_2 polyhedral chain readily fits into the SWNT capillary.

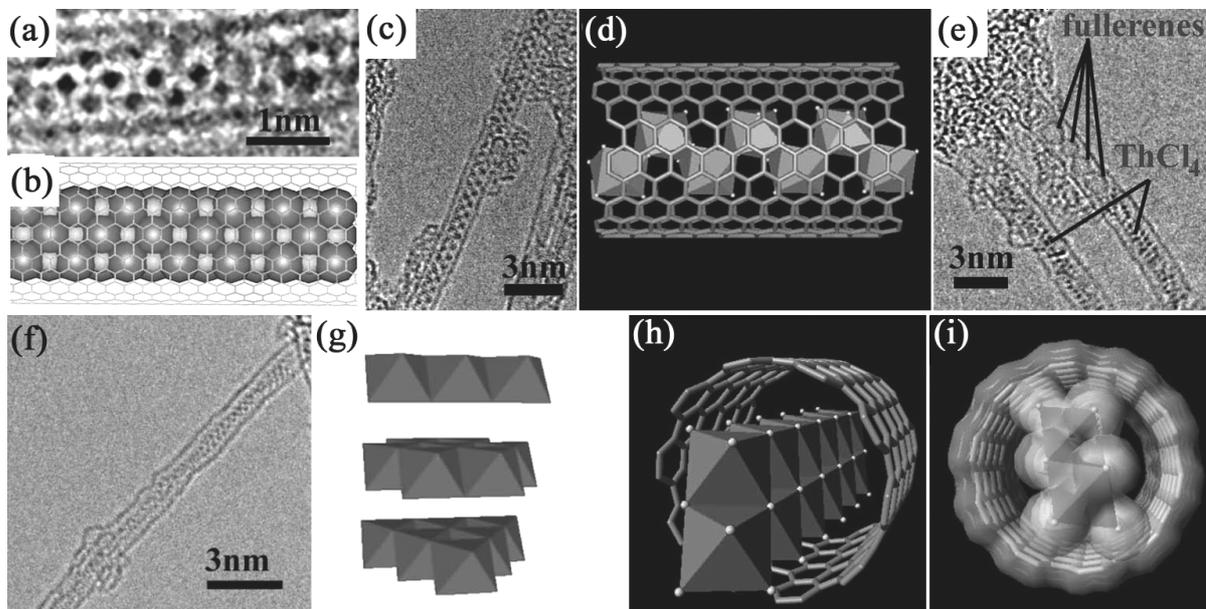


Figure 1. (a) HRTEM image of a crystal of CsCl formed within a SWNT. (b) Schematic representation of a possible structural interpretation of the obtained filling. (c) and (d) HRTEM image and idealised structural representation of KCl/ThCl_4 formed within a SWNT. (e) Fullerenes impeding KCl/ThCl_4 crystal growth within a SWNT. (f) HRTEM image showing a 'twisted' crystal of CdCl_2 formed within a SWNT. (g) Bulk layered structure of CdCl_2 . (h) Idealised structural representation of CdCl_2 formed within a SWNT. (i) van der Waals surface of SWNT/ CdCl_2 encapsulate.

3. Conclusion

SWNTs are ideal model environments for imaging low dimensional materials that are just a few atomic layers in thickness. The obtained structures are among the thinnest crystals known and represent a significant challenge for HRTEM.

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References

- [1] J. Sloan, J. Hammer, M. Zweifka-Sibley, M.L.H. Green, *Chem. Commun.*, **1998**, 347.
- [2] J. Sloan, D.M. Wright, H.G. Woo, S. Bailey, G. Brown, A.P.E. York, K.S. Coleman, J.L. Hutchison, M.L.H. Green, *Chem. Commun.*, **1999**, 699.
- [3] J.L. Hutchison, R.C. Doole, R.E. Dunin-Borkowski, J. Sloan, M.L.H. Green, *JEOL News*, 1999, 34E, 10.
- [4] J. Sloan et al., submitted.
- [5] J. Sloan, R.E. Dunin-Borkowski, J.L. Hutchison, K.S. Coleman, V.C. Williams, J.B. Claridge, A.P.E. York, C. Xu, S.R. Bailey, G. Brown, S. Friedrichs and M.L.H. Green, *Chem. Phys. Lett.*, **2000**, 316, 191.
- [6] B.W. Smith, M. Monthieux and D.E. Luzzi, *Nature*, **1998**, 396, 323.