# HRTEM studies of alkali halides incorporated into single walled carbon nanotubes

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**Summary:** The HRTEM of single walled carbon nanotubes (SWNTs) filled with alkali halides is described. Lattice images revealed different types of packing within the SWNT capillaries. In thinner capillaries, most crystals showed a preferred orientation and formed in a crystallographically aligned fashion along the nanotube capillaries.

## 1. Introduction

Metal halides may be introduced into single walled carbon nanotubes (SWNTs) by capillarity [1-2]. These experiments permit the study of low dimensional crystal growth whereby the incorporated material is constrained by the encapsulating van der Waals surface of the incorporating capillaries, to a few atomic layers in thickness. Alkali halides restricted to MX with M = Li, Na, K, Rb and Cs and X = Cl, Br, I provide a useful model system to gauge the crystal growth behaviour and imaging properties of metal salts incorporated into SWNTs because of their relatively simple structure types and because of the ability to tailor the imaging properties of the halide by varying the respective constituent anions and cations [3].

## 2. Experimental

SWNTs were prepared using the high yield catalytic arc synthesis method described by Journet et al. [4] and the nanotubes were filled in high yield by the capillary wetting technique described elsewhere [2,3]. The SWNT samples were examined at 300 kV in a JEOL JEM-3000F FEGTEM, which has a low spherical abberation coefficient $C_s$ of 0.6 nm and a point resolution of between 0.16 nm. Images were acquired digitally onto a Gatan model 794 1k × 1k CCD camera at an accurately calibrated magnification.

## 3. Results and discussion

In Figure 1 we show examples of different types of packing observed within SWNTs. Fig. 1(a) shows the packing of six atomic thick layer NaI crystal formed within a wide (*ca.* 2.3nm diameter) SWNT. In projection the lattice image and inset Fourier transform (FT) indicate that the crystal is imaged along $[\bar{1}01]$ relative to the parent F*m*3*m* NaI phase. In this projection, the dark spots correspond to iodine columns only, the interstitial Na columns contributing negligible contrast to the lattice image. When alkali halides with heavier cations and lighter anions where imaged iside SWNTs (e.g. Cs or Rb chlorides), then the contribution from the heavier cation lattices was found to dominate the lattice images obtained from similar projections.

The two KI crystals in Figs.1(b) and (c) are both imaged along [100] with respect to the parent structure and both show well-defined square lattices arranged in a preferred orientation along the SWNT axes. In the lower right of Figure 1(b), the incorporated material forms a continuous

ordered crystallite which is just three atomic layers thick, formed inside the SWNT capillary, measured at 1.6nm in diameter. In this case, the prominent dark spots correspond to alternating K-I-K or I-K-I columns imaged in projection. Rows of the dark spots are separated by *ca*. 0.322nm, corresponding to the (200) spacing of bulk KI. At the left of the micrograph, the imaged crystal is less well ordered and the square lattice is no longer visible. It is noteworthy that the diameter of the tubule is less at this point (ca. 1.4nm), suggesting either a twist in the crystal or a distortion in the SWNT (possibly inter-related). In Fig 1(c) we see another example of a KI crystal formed within a SWNT. The diameter of the SWNT varies sharply and in the thinner (1.6nm diameter) region, a three layer KI crystal is visible. At the lower end of the tubule, this region of crystal terminates. In the wider-diameter region (2.75nm diameter) of the SWNT, a much thicker region of KI crystal is visible. Although the well-defined image contrast of the columns in the lower left of the crystal is no longer visible, we can estimate that this thicker region corresponds to a seven layer thick crystal of KI.

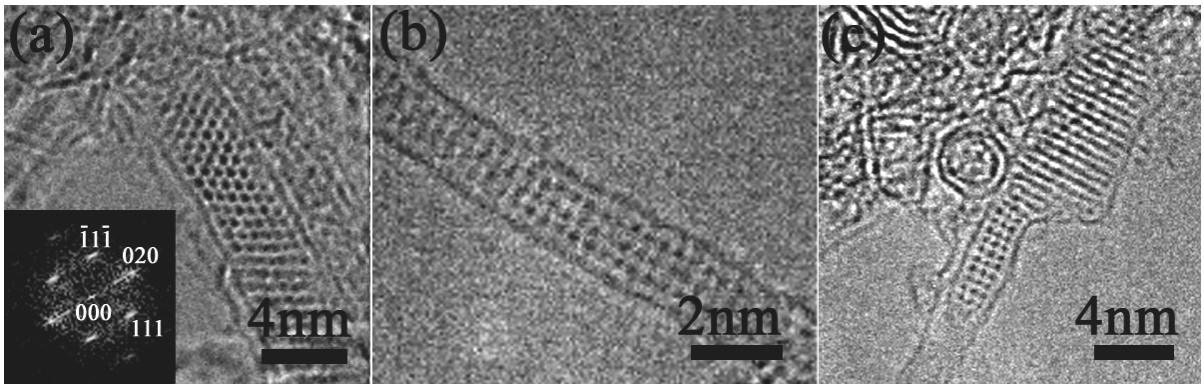


Figure 1 (a) HRTEM image of NaI crystal within a large diameter (ca. 2.5nm) SWNT. The lattice image and inset FFT obtained from the lattice image indicates that the incorporated crystal is a $[\bar{1}01]$ projection of NaI. (b) Lattice image of a three atomic thick crystal of KI incorporated into a 1.6nm (12,12) SWNT. (c) HRTEM image showing a terminating KI crystal (viewed along [100]) incorporated into a 1.6nm SWNT widening into a 3.6nm tubule. The incorporated KI crystal is three layers thick in the thin region and seven layers thick in the wider region.

## Conclusions

The incorporation of alkali halides within SWNTs permits the study of relatively simple 3D structures which form in a comparatively predictable fashion within SWNTs. As such, these composites represent valuable model materials for investigating low dimensional crystal growth behaviour. As HRTEM specimens, these structures are extremely valuable as they are structures which have a known, exact number of atomic layers in thickness.

## References

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