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High yield incorporation and washing properties of halides incorporated into single walled carbon nanotubes

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ABSTRACT We describe here the high yield filling (i.e. > 50%) of single walled nanotubes (SWNTs) with a variety of halides, achieved according to various modified filling procedures. Both bundles and discrete SWNTs can be filled continuously up to lengths of several hundred nm, often with filling yields approaching 60–70% or better. In addition some high yield filled SWNTs were subjected to long-term washing in either boiling or room temperature. aqueous media, which does not remove the filling from the tubules, but enables effective removal of water-soluble extraneous materials .

PACS 81.07.De; 61.46.+w; 68.37.Lp

1 Introduction

Single walled carbon nanotubes (SWNTs) [1, 2] can be filled with binary solid phase materials by solution-deposition, [3] capillarity [4, 5] and by diffusion of molecular species, such as fullerenes [6, 7] or endofullerenes [8, 9] into raw, heat-treated or vacuum annealed [7–9] SWNTs. Where SWNTs have been filled using ionic crystalline melts, nano-scale crystals with precise integral layer architectures (i.e. 'Feynman Crystals') can be formed [10]. The structural properties of the inserted 1D crystals are principally dictated by the structural chemistry of the bulk material, although deviations from bulk crystal growth behaviour and structures are observed. Alternatively, encapsulated 1D crystals with completely novel structures can form, as recently observed for 1D chains of BaI_2 formed within 1.6 nm diameter SWNTs [11]. Ternary or higher-order mixtures of halides may also be inserted into SWNTs by exploiting the melting properties of the phase diagram corresponding to the components of the material to be introduced. For example, mixtures of AgCl-AgBr, KCl-UCl_4 and AgCl-AgI may be introduced into SWNTs [5, 12]. In the case of the latter, a solid crystalline solution of the form $AgCl_{1-x}I_x$ was observed to form within the SWNT capillaries [12]. Finally, it is now also possible to determine the chirality of the host tubule simultaneously with inclusion crystallography [13], an essential step toward

the full ab initio determination of the physical properties of particular SWNT nanocomposites. This follows from the relationship between tubule chirality and the metallic or semiconducting properties of the encapsulating tubule [14].

The synthesis of filled SWNT composites is expected to result in nanomaterials that have considerably modified physical properties relative to unfilled tubules, including enhanced semiconducting or metallic conductivity, quantum wire-like behaviour and so forth. From the point of view of the effective characterisation and further development of these materials, the synthesis of quantitatively filled SWNT nanocomposites must be considered to be of paramount importance. Furthermore, it is also vital that any extraneous filling material be removed following synthesis in order that any physical measurements may be directly attributable to the nanocomposite materials. In this article, we present a number of examples of high-yield filled SWNT composites and also present results concerning the washing properties of one of these filled composites. In this article "high yield" means observed filling yields estimated at 50% or higher.

2 High yield filling of SWNTs with resublimed $ZrCl_4$

$ZrCl_4$ is a low melting material with a melting point of 711 K and which exhibits an extraordinarily low surface tension of 1.3380 $mN\,m^{-1}$ when molten in the temperature range 715–760 K (Table 1) [5]. This value is well below the threshold surface tension of 200 $mN\,m^{-1}$ specified by Ebbesen for the efficient wetting and filling of multiple walled carbon nanotubes (MWNTs). Two syntheses of $ZrCl_4$/SWNT composites were attempted. The first was performed by heating to 623 K a 1 : 1 mixture by weight of SWNTs with the as-supplied halide and the second by repeating the same procedure with resublimed $ZrCl_4$. In general, the filling of SWNTs was achieved without recourse to a separate opening step, which was initially thought to be necessary [3]. This is consistent with our observations for the filling of SWNTs with halides from the KCl-UCl_4 and AgCl-AgBr systems [5]. The filling procedure used for this experiment is described elsewhere [5].

In Fig. 1a and b high-resolution transmission electron microscopy (HRTEM) images showing the filling product obtained from the as-supplied $ZrCl_4$ can be seen. At the top of

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Salt	$T_m(K)$[a]	$T_f(K)$[b]	$g = a - bT$ (mN m^{-1})	Temp. Range (K)	S.T.[c] at T_f (mN m^{-1})	Est. filling yield
ZrCl$_4$	710	760	80.91–0.1047T	715–760	1.34	50–60%
LiI	722	822	140.7–0.0565T	870–1100	94.25	< 10%
NaI	934	1034	139.83–0.0573T	945–1165	80.58	10–20%
KI	954	1054	136.1–0.06003T	969–1186	69.62	40–50%
RbI	920	1020	132.89–0.0614T	921–1125	70.25	60–70 + %
CsI	899	999	125.9–0.0567T	930–1070	69.26	30–40%
AgCl	833	933	134.08–0.023T	773–873	112.67	40–50%
AgBr	705	805	171.3–0.025T	733–893	151.18	40–50%
AgI	728	828	214.4–0.052T	733–973	171.34	40–50%
UCl$_4$	863	963	204.95–0.185T	1123–1323	26.80	< 10%
BaI$_2$	1013	1113	177.2–0.042T	1099–1231	130.45	< 10%
CaI$_2$	1057	1157	103.4–0.0173T	1068–1325	83.38	< 10%
KCl-UCl$_4$[d]	835	935	77.59–0.01349T	870–1050	64.97	< 10%
KCl-UCl$_4$[e]	608	708	102.83–0.0621T	890–980	43.97	< 10%
AgBr$_{0.2}$Cl$_{0.8}$	683	783	205.3–0.04182T	773–873	172.55	40–50%

TABLE 1 Comparative surface tension data [15] and observed filling yields for a representative group of halides and mixtures of halides introduced into SWNTs. Surface tensions were calculated within the specified temperature ranges according to the relation $g = a - bT$, where g is the surface tension, T the absolute temperature and a and b are constants

a: T_m = melting temperature; b: T_f = filling temperature; c: S.T. = calculated surface tension; d: eutectic I (73.2 mol % KCl: 26.8 mol % UCl$_4$); e: eutectic II (39.33 mol % KCl:30.67 mol % UCl$_4$)
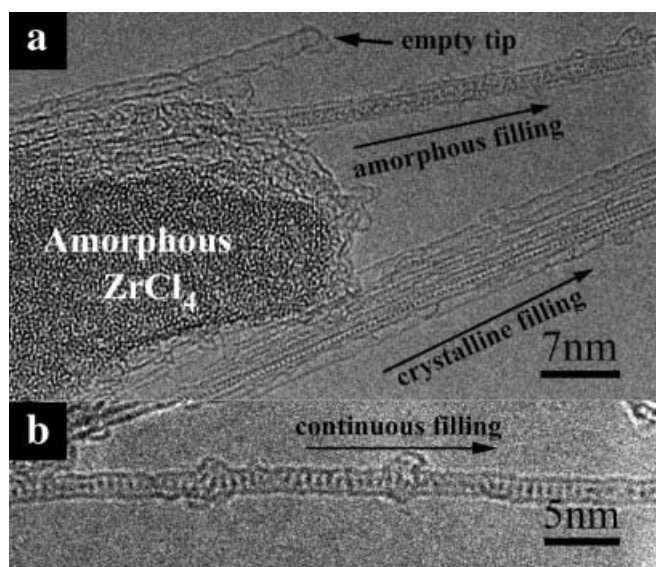

FIGURE 1 **a** Unfilled SWNT tip, SWNT filled with amorphous ZrCl$_4$ and a partially filled SWNT bundle. Note amorphous ZrCl$_4$ formed on outside of SWNTs. **b** HRTEM image of a discrete SWNT continuously filled with ZrCl$_4$. Note the banded nature of the incorporated microstructure (cf. amorphous material in **a**). Energy dispersive X-ray microanalysis spectra (not shown) confirmed that the filling material was ZrCl$_4$
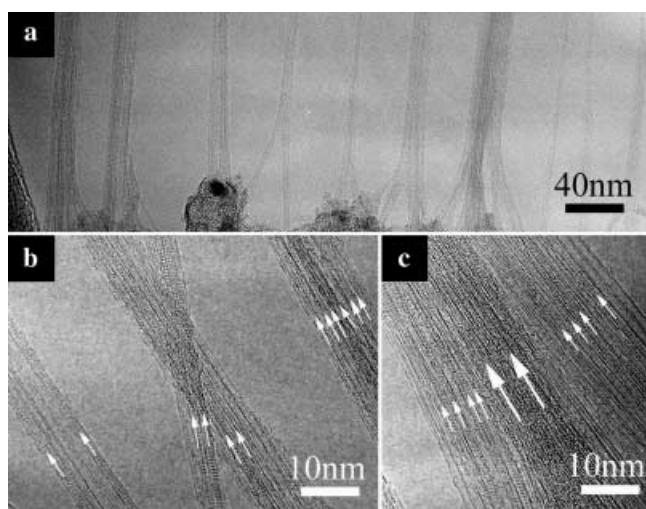

FIGURE 2 **a** Array of SWNT bundles observed stretched across a gap in the holey carbon film of a HRTEM support grid. **b** Micrograph showing four SWNT bundles partially filled with ZrCl$_4$. *Arrows* indicate regions of filling. **c** Micrograph showing a large, partially filled SWNT bundle. *Small arrows* indicate individual filled SWNTs while the *large arrow* indicates the densely filled region

Fig. 1a, an empty SWNT tip is indicated. Below this, a pair of overlapping SWNTs, one of which is apparently filled continuously with amorphous ZrCl$_4$, is visible. At the bottom of the micrograph, a bundle of 8–10 SWNTs, one of which is filled with crystalline ZrCl$_4$, is visible. In Fig. 1b, a discrete 1.1 nm diameter SWNT, completely filled with crystalline material, is visible as a continuous 1D banded structure with the bands spaced at ca. 0.48 nm intervals. To the centre left of Fig. 1a, ZrCl$_4$ external to the SWNTs can be seen. This material invariably appeared to be amorphous, although it was observed to 'jiggle' in the 400 kV electron beam, indicating that its appearance is possibly due to the presence of water molecules in the filling. Crystalline ZrCl$_4$ observed within SWNTs only loses crystallinity upon continuous exposure to the electron beam for several minutes.

Upon continued exposure, this material dissociates into discrete ZrCl$_x$ clusters, as reported elsewhere [17]. The average filling yield in this sample was estimated to be between 20–30%.

In Fig. 2a–c, examples of the ZrCl$_4$ fillings obtained with resublimed ZrCl$_4$ can be seen. Figure 2a shows an array of several bundles of SWNTs stretched over a gap in the carbon film of the HRTEM support grid. Each bundle contained a significant proportion of ZrCl$_4$-filled SWNTs, as shown by the enlargements in Fig. 2b and c. In Fig. 2b, four partially filled SWNT bundles are visible while, on the left, a bundle of SWNTs can be seen with two peripheral nanotubes filled with ZrCl$_4$ (white arrows). To the right of this, three other bundles with relatively higher amounts of filling are indicated. In Fig. 2c, a large bundle of SWNTs observed with filling is shown. Towards the periphery, paths of individual SWNTs containing filling are indicated (small white arrows). In the

centre of the bundle, a dense region of filling is shown (large white arrows). The average degree of filling in this sample was estimated as 50–60%. A significant overall increase in filling yield was therefore obtained by use of an ultra-pure resublimed filling material.

3   Comparative filling yields of binary halides as a function of surface tension properties

We have engaged in a systematic study of the filling and crystallisation properties of various binary halides as a function of bulk structure type and respective imaging properties [10]. Given the wide range of varying structural complexity exhibited for halides over different stoichiometries [18], it is perhaps only appropriate to compare melting properties within a group and for a given structure type. To address this we have filled samples of SWNTs prepared using comparable filling conditions (i.e. at least in terms of surface tension) with five different alkali iodides (i.e. MI with M = Li, Na, K, Rb and Cs). Iodides were chosen in order that all of these halides could be imaged due to the strongly scattering counter-ion. The filling technique used was that referred to above [5] and the SWNTs were prepared according to a previously described high-yield synthesis procedure [19]. The halides were ground together with identical samples of as-prepared SWNTs and then heated in silica quartz ampoules sealed under vacuum to 100 K above the melting temperature of the respective halides. The melting [20] and calculated surface tension [15] properties of the respective halides, together with the estimated filling yields (i.e. the number of SWNTs observed with filling) of the five iodides are reproduced in Table 1. We also reproduce similar data for a representative range of other binary and ternary halide systems that we have introduced into SWNTs for comparison.

An interesting feature concerning the obtained filling yields was that they were found to be somewhat independent of the calculated surface tensions. KI, RbI and CsI all exhibit roughly similar surface tensions at the filling temperature employed (Table 1) but only RbI exhibited a particularly high filling yield. While LiI and NaI have slightly higher surface tensions at the filling temperatures employed, this discrepancy is insufficient to account for the low filling yields obtained in each case. Comparisons with and between other filling systems (Table 1) also indicate a rather poor correspondence between the observed filling yield and surface tension. In particular the lowest surface tension filling material employed (i.e. $ZrCl_4$; 1.34 mN m^{-1} at 760 K) shows approximately the same overall filling yield as the highest (i.e. $AgBr_{0.2}Cl_{0.8}$; 172.55 mN m^{-1} at 683 K) at a considerably lower temperature. These results suggest that, while essential in terms of actually obtaining filling [16], low surface tension alone is not of itself a strong factor in terms of determining the overall obtained filling yield.

HRTEM images showing examples of SWNT bundles filled with LiI, NaI and CsI are presented in Fig. 3a, b and c, respectively. The inset details show the high crystallinity of the obtained fillings but, in all cases, the amount of filling per bundle is less than 30%. In the case of KI (see Fig. 5a, below) a higher filling yield of 50% was observed per bundle but this was not as dramatic as observed for RbI as can be
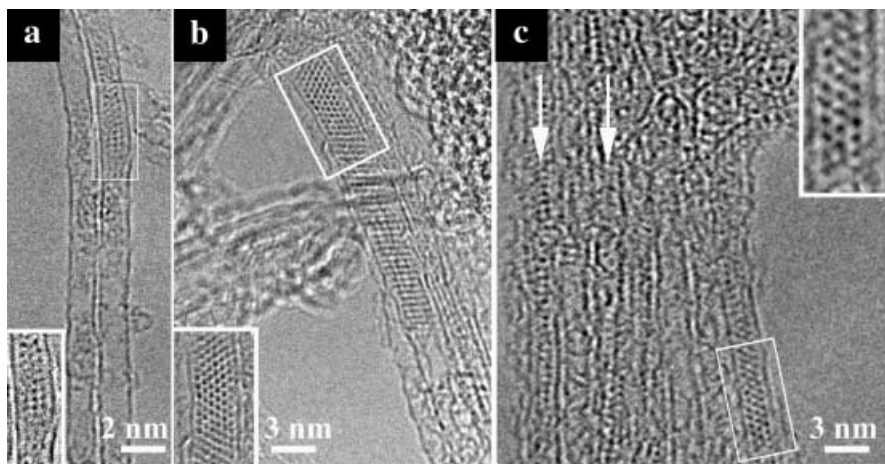

FIGURE 3   **a** HRTEM micrograph showing a pair of SWNTs. Enlargement from boxed region (*inset*, ×2) shows a small quantity of rocksalt LiI filling. The Li in this image is effectively visible – the *dark spots* due to the iodine sublattice. **b** HRTEM micrograph and *inset* enlargement (×2) showing a wide-bore SWNT within a bundle of SWNTs filled with NaI. **c** HRTEM micrograph showing a bundle of SWNTs 1/3 filled with CsI. An enlargement of the boxed region (*inset*, ×2) shows crystalline CsI filling in a peripheral SWNT
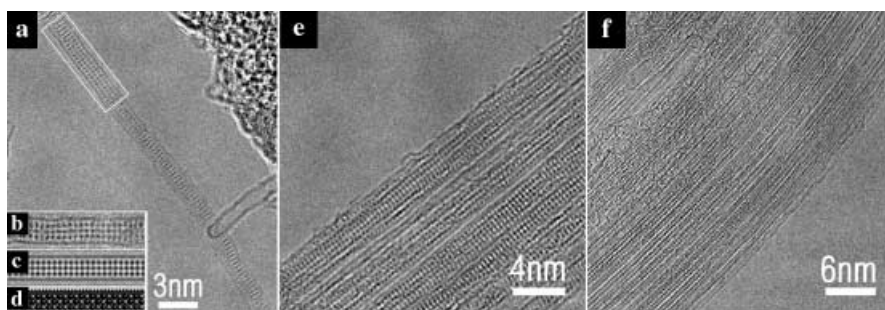

FIGURE 4   **a** Micrograph showing a discrete 1.6 nm diameter SWNT filled with a 3×3 crystal of RbI. **b**, **c** and **d** ×2 enlargement of boxed region in **a**, Scherzer focus image simulation and structure model (Rb = *white spheres*, I = *dark spheres*, C = *grey spheres*). **e** and **f** HRTEM micrographs showing SWNT bundles almost quantitatively filled with RbI
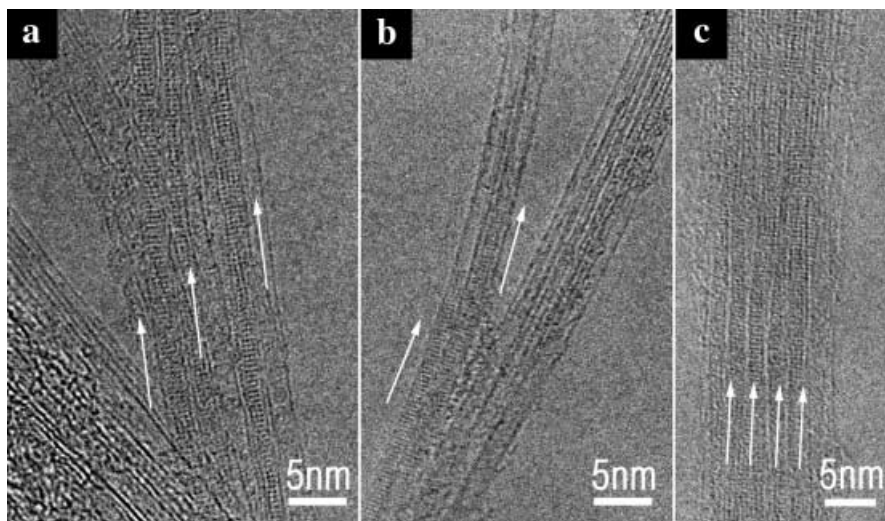
FIGURE 5 **a** As-prepared SWNT bundle filled with KI prior to washing treatments. The estimated filling yield is 50%. **b** Partially filled bundle observed after boiling composite material in water for three days. **c** Filled SWNT bundle observed after the same sample was left immersed in water at room temperature for a total of 90 days

seen in Fig. 4. Figure 4a–d show evidence for the formation of a 3×3 RbI crystal within a discrete 1.6 nm diameter SWNT. The microstructure of this material corresponds closely to that which we have reported for 2×2 and 3×3 KI crystals formed in 1.4 nm and 1.6 nm diameter SWNTs [21, 22]. The high filling yield obtained in the rest of the specimen is reflected in the observation of quantitatively filled SWNT bundles (Fig. 4e and f) which were predominant in the sample.

4   Washing properties of KI within SWNTs

Selected samples were used to test the washing properties of the alkali halides within SWNTs using the same literature techniques cited above for the filling and preparation of nanotubes [5, 19]. A sample of SWNTs was filled with KI, achieving a filling percentage of 30–50%. This sample was stirred in boiling water for three days and then left suspended, at room temperature, for a further 90 days. Two samples were taken from this sample and then dried for HRTEM observations after the initial three days and then after the full 90 days, respectively.

Although it was difficult to provide a truly quantitative estimate of remanent filling from HRTEM imaging alone, it was apparent that relatively little KI had been removed from the sample. Figure 5a shows a HRTEM image of a typical SWNT bundle exhibiting ca. 50% filling. Figure 5b and c show HRTEM images obtained from the three day and 90 day washed samples, respectively. The white arrows, pointing along the axes of the tubules, indicate clearly that the SWNT tubules are still filled with KI. The left group of tubules in Fig. 5b show partial filling that terminates in the middle of the SWNTs, which may indicate that these fillings are undergoing partial solvation. However, this is difficult to verify without being able to observe the washing process in situ. In Fig. 5c, a filled bundle observed in the sample soaked for 90 days is shown. Luzzi [23] has reported that lanthanide halides are similarly resistant to solvation upon SWNT incorporation.

One explanation for the failure of KI (or lanthanide halides) to wash out of SWNTs is that they may seal (or reseal) during cooling, thus inhibiting the access of the aqueous media to the crystals. However, given that the SWNTs may be at least partially open either at their ends [19] or at the loci of side wall defects, the failure of the halides to dissolve may also be indicative of the difficulty of forming an effective solvation sphere within the confines of a SWNT capillary. It may be possible to leach out K^+ and I^- species slowly from the ends of the 1D crystals exposed to solvents and, indeed, the partial filling visible in Fig. 5b may indicate this. However, another explanation for the terminating filling in Fig. 5b may be the fact that this particular filling had solidified and simply come to a dead stop, as we have noted for other partially filled SWNTs.

5   Procedures for high yield filling of SWNTs with CdTe-CdBr$_2$ mixtures

In most of the prior capillary filling experiments described in this laboratory, a filling procedure was used in which a relatively simple heating regime was used to introduce binary halides [5, 10, 11, 13, 17, 21, 22], ternary halides [5, 12], oxides [13] and mixed halides-chalcogenides [24] into SWNTs. This procedure normally involves a simple ramp-dwell-cool cycle in the case of the binary materials (i.e. Fig. 6, scheme **I**). In the case of ternary phases, a pre-melting step is generally employed to ensure homogeneity of the sample prior to the filling experiment [5, 10, 12]. Furthermore, in the experiments chosen to date, homogeneous crystalline filling was only obtained in the case of eutectic compositions, as observed in the case of partially miscible systems.

Two common problems exhibited by many of the ternary systems introduced into SWNTs were generally low filling yields and poor crystallinity of the filling material. For example, the case of a KCl-UCl$_4$ mixture introduced into SWNTs, less than 10% filling was observed and much of the obtained filling was glassy [5]. In order to combat these problems, we have introduced some modifications to the filling procedure, as indicated in Fig. 6, schemes **II** and **III**. The first modification was the introduction of an anneal step (i.e. scheme **II**) in which the samples were subjected to a prolonged anneal at a temperature 100 K below the melting tem-

perature following the initial filling step. A second modification was to cycle the dwell and anneal steps, the idea being that these would improve the overall filling yield observed in the samples. Additionally we also increased the lengths of time the samples were effectively in the presence of molten media by up to 1000%.

The extended filling periods, anneals and thermal cycles were shown to be at least partially effective in improving the proportion of filled tubules observed within a treated SWNT sample. In Fig. 7a and b, HRTEM images show filling of $CdBr_{2-x}Te_x$ introduced into SWNTs using schemes **II** and **III** respectively. Improvements in crystallinity were apparently observed where **II** was employed alone and an improvement in filling yield of about 10–20% was also observed in samples in which the composite material was thermally cycled.

Improvements in terms of the filling yields of fullerenes or endofullerenes introduced into SWNTs from the gas phase
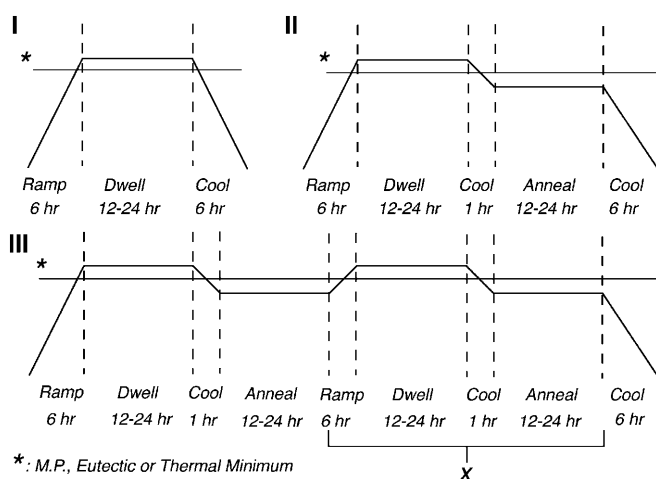
have been reported [8, 9]. In these cases the nanotubes were either pre-heated in dry air [8] or annealed in vacuo [9] at temperatures in the range 673–723 K. We have attempted to use these procedures to quantitatively fill SWNTs with solid phase materials but, to date, little improvement in the overall filling yield has been observed for any of the systems studied.

6   Conclusions

We have reported various methods for improving the filling yield of SWNTs incorporating halides, mixtures of halides and mixtures of halides together with chalcogenides. While it is clear that other factors need to be taken into account, for example, the rate of opening of the SWNTs (assuming that this is not promoted or caused by contact with molten media), it is clear the relative purity of the filling material and the heating regime employed can influence the rate of filling. Another important observation is that, given comparable filling conditions, some alkali iodides with comparable surface tensions show superior filling properties to others, suggesting that additional factors may be at play (e.g. structural factors) which influence filling yields. A further experimental observation is that we have shown that alkali halides contained within SWNTs show a clear resistance to solvation by aqueous media.

FIGURE 6   Heating regimes employed for filling SWNTs with binary or ternary compounds. **I** Simple ramp-dwell-cool regime. **II** Simple heating regime incorporating an anneal step to improve filling crystallinity. **III** Cycled heating regime employing multiple dwell and anneal steps. The cycle x may be repeated several times in order to achieve incremental improvements in filling yield. Note that the Dwell and anneal temperatures are approximately 100 K above and 100 K below the indicated melting (or liquidus) temperatures, respectively
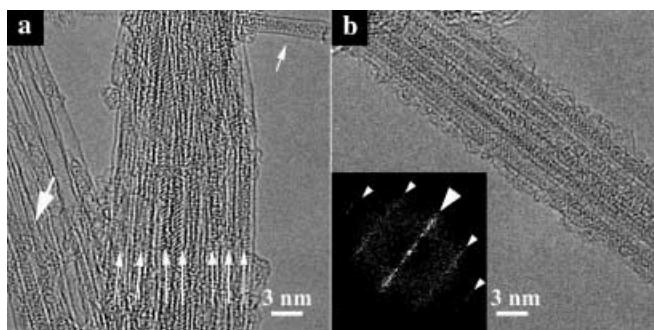

FIGURE 7   HRTEM micrograph showing a near-quantitatively $CdBr_{2-x}Te_x$–filled SWNT bundle (*centre*) and a partially filled SWNT bundle (*left*). The *arrows* indicate the presence of filling. A discrete filled SWNT is indicated at the *upper right*. This sample was filled using regime **II**. **b** HRTEM micrograph showing a SWNT bundle quantitatively filled with $CdBr_{2-x}Te_x$ (regime **III**). An idea of the relative crystallinity can be obtained from the *inset* power spectrum. The *large arrows* correspond to scattering from the SWNT while the *smaller arrows* indicate scattering due to filling

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