High yield incorporation of $ZrCl_4$ into single wall carbon nanotubes imaged by HRTEM

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Summary: The filling of single walled carbon nanotubes (SWNTs) with $ZrCl_4$ in high yield is reported. Both bundles and discrete SWNTs were filled continuously with up to 60-70% of observed nanotubes filled continuously with orientated crystalline $ZrCl_4$. HRTEM imaging showed that the $ZrCl_4$ formed as 1D-chains within the SWNT capillaries.

1. Introduction

Single walled carbon nanotubes (SWNTs) can be filled by solution-deposition [1] or by capillarity [2]. The latter may be achieved by the use of molten metal halides or mixtures of metal halides. The synthesis of filled SWNTs is expected to produce low dimensional materials with considerably modified physical properties. To further the efficient characterisation and development of SWNT filling, the synthesis of high yield nanocomposites may be considered to be of paramount importance. Here we describe the high yield insertion of $ZrCl_4$ into SWNTs. $ZrCl_4$ exhibits an extremely low surface tension when molten above its m.elting point of 711K. The values, which are 6.0495mNm^{-1} at 715K and 1.3380mNm^{-1} at 760K, are well below the threshold surface tension of 200mNm^{-1} suggested for successful wetting and filling of multi-wall nanotubes [3].

2. Experimental

SWNTs were prepared using the high yield catalytic arc synthesis method [4]. the nanotubes were filled in high yield by the capillary wetting technique described elsewhere [2,3]. Each mixture was sealed *in vacuo* in a silica ampoule and heated at 2K/min to 623K in a furnace, held at temperature for 1hr and then furnace cooled. The specimens were characterised using a JEOL 4000EX(II) HRTEM (400kV) and a JEOL 3000F FEGTEM (300kV) equipped with a LINK 'ISIS' EDX system. Microanalysis was performed with a 0.5nm diameter electron probe.

3. Results and discussion

Figure 1(a) and 1(b) show the filling product obtained from as-supplied $ZrCl_4$. Figure 1(a) shows an empty SWNT tip. Below this are a pair of overlapping SWNTs, one continuously filled with amorphous $ZrCl_4$. At the bottom of the micrograph, a bundle of SWNTs, two filled with crystalline $ZrCl_4$, are visible. In Figure 1(b) a discrete SWNT completely filled with crystalline material is visible. This material displays a continuous 1D structure with imaged dark bands spaced at *ca.* 0.48nm intervals. This shows unequivocally that $ZrCl_4$ is incorporated into the SWNT capillary and is not a feature of surface wetting. To the left of Figure 1(a) extraneous $ZrCl_4$ filling material is visible. This appears amorphous, although this appearance may possibly be beam induced. All of the incorporated $ZrCl_4$ eventually lost crystallinity upon prolonged exposure to the electron beam. The average filling yield for 'as-supplied' $ZrCl_4$ was estimated to be between 20-30%.

In Figures 2(a)-(c), $ZrCl_4$ fillings obtained with sublimed $ZrCl_4$ are shown. Figure 2(a) shows an array of several bundles of SWNTs stretched over a gap in the HRTEM carbon support film. Each of these bundles was found to contain a significant proportion of filled SWNTs as shown by the enlargements in Figures 2(b) and (c). Figure 2(b) shows four partially filled SWNT bundles. On the left, a bundle of SWNTs can be seen with two continuously filled nanotubes indicated by the white arrows. To the right of this, three bundles with high levels of filling are indicated. In Figure 2(c), a large bundle of SWNTs with filling is shown. The paths of individual filled SWNTs are indicated by white arrows. In the centre, a dense region of filling is seen in which the paths of individual filled SWNTs are obscured. The average filling yield in this sample was estimated at 50-60%.

The composition of the filling obtained with purified $ZrCl_4$ was verified by EDX and in Figure 3, a spectrum obtained from a bundle of $ZrCl_4$ filled SWNTs is shown. The Zr Lα peaks and Cl Kα peaks are clearly visible, as is a weak carbon peak at 0.282 KeV.

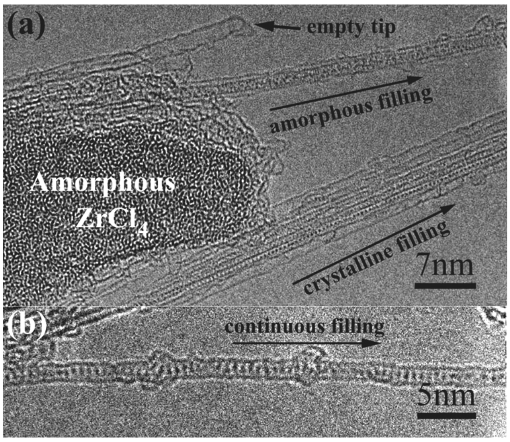

Figure 1(a) Unfilled tip, SWNT filled with amorphous $ZrCl_4$ and partially filled SWNT bundle. (b) HRTEM image of a discrete SWNT continuously filled with $ZrCl_4$. Note the banded nature of the incorporated microstructure.

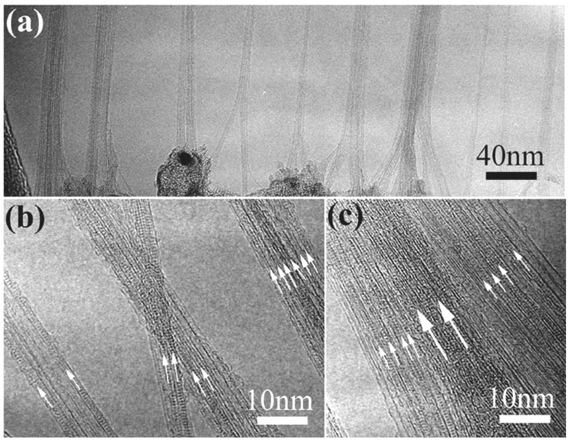

Figure 2(a) Array of SWNT bundles observed stretched across a gap in the holey carbon film of a HRTEM support grid. (b) Micrograph showing four SWNT bundles partially filled with $ZrCl_4$. (c) Micrograph showing a large, partially filled SWNT bundle.

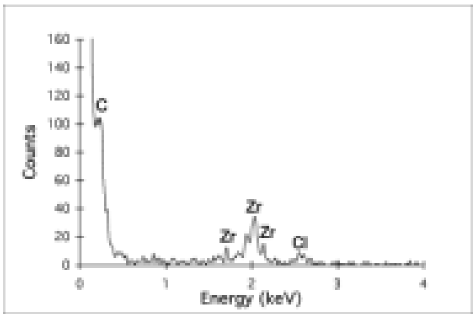

Figure 3 (left) EDX spectrum obtained from a SWNT bundle filled with $ZrCl_4$.

4. Conclusion

In summary, we have described a simple procedure for the high yield incorporation of $ZrCl_4$ into SWNTs. The structure of the SWNT incorporated $ZrCl_4$ is thought to be derived from the chain structure of the bulk material and is the subject of continued investigations in this laboratory.

References

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