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Direct imaging of *o*-carborane molecules within single walled carbon nanotubes

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***Ortho*-carborane molecules have been inserted into single walled carbon nanotubes (SWNTs) and imaged directly by high resolution transmission electron microscopy (HRTEM); both discrete molecules and 'zig-zag' 1D chains of *o*-carborane 'petit pois' were observed to pack into the tubule capillaries.**

In the same year that the first foreign material was encapsulated within single walled carbon nanotubes (SWNTs),[1] Smith *et al.* found that tubules prepared *via* pulsed laser vapourisation (PLV) contained close-packed 1D chains consisting of C_{60} and other fullerene molecules (*i.e.* C_n), termed 'peapods' or, more formally, C_n@SWNTs.[2] Subsequently, quantitative filling of SWNTs with specific fullerenes was achieved[3] followed by incorporation of endofullerenes, resulting in [La_2@C_{80}]@SWNT[4] and [Gd@C_{82}]@SWNT[5] composites. Scanning tunnelling microscopy (STM) studies performed on C_{60}@SWNT[6] and [Gd@C_{82}]@SWNT[7] reveal significant band-gap modulations, lending credibility to the argument that similar composites could form components in devices such as a solid-state quantum computer[8] or a quantum cascade laser.[9] We have now extended this filling chemistry to boron-containing molecular species and report here the imaging and packing properties of *o*-carborane molecules inserted into SWNTs.

Ortho-carborane (1,2-dicarbododecaborane) has the molecular formula $(CH)_2(BH)_{10}$ and consists of an icosahedral cluster of C_2B_{10} with hydrogen atoms attached at the vertices, in a structure analogous to borane or $(B_{12}H_{12})^{2-}$.[10] In the bulk, this structure crystallises in a *fcc* lattice[10] in which the lattice points are occupied by entire molecules as is the case for C_{60}.[11] At rt, these molecules rotate rapidly, as shown by NMR,[10] and may thus be regarded as spheres 0.81 nm in outside diameter (Fig. 1(a)) as compared to an analogous diameter of 1.0 nm for C_{60} molecules (Fig. 1(b)).[10] HRTEM image simulation studies (Fig. 1(c) **I**–**IV**) show that the imaging properties of individual *o*-carborane molecules are fundamentally different to those of the fullerenes and image as blurred spots corresponding to 12 weakly scattering atoms (*i.e.* C and B) arranged in a tightly packed cluster (Fig. 1(c), top) rather than as dark circles (Fig. 1(c), bottom) corresponding to C atoms arranged in a 0.7 nm sphere as for C_{60}.[12]

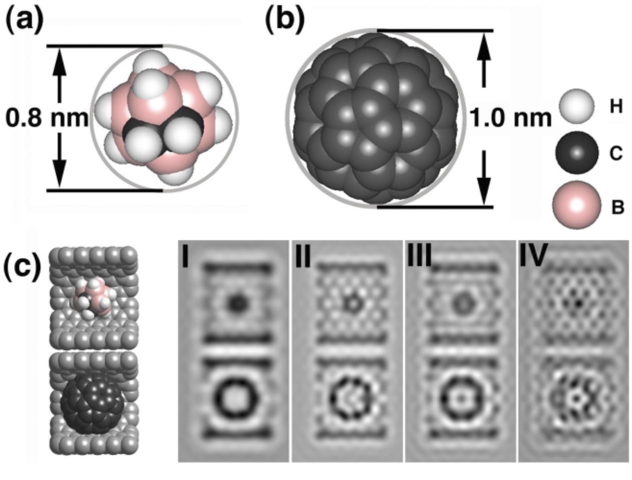

Fig. 1 (a) and (b) space filling models of *o*-carborane and C_{60} molecules with outside diameters at rt indicated (c) space filling models (left) of *o*-carborane (top) and C_{60} inside a (10,10) SWNT fragment and corresponding computed focal series (**I** −49 nm; **II** −39 nm; **III** −29 nm; **IV** −19 nm defocus).

Samples of SWNTs were prepared by a modified catalytic arc synthesis route.[12] Selected samples were subjected to acid treatments (*i.e.* shaking in 35% HCl at rt followed by washing and oven drying) to assess the impact on filling yield. For each experiment, ~50 mg SWNTs together with ~100 mg of *o*-carborane were ground together and transferred to a quartz ampoule in a dry box. The ampoule was sealed under vacuum and then heated to 350 °C in a tube furnace. For the later runs the SWNTs were heat treated first at a temperature of 420 °C under a dynamic flow of 20% O_2/80% Ar for 20 minutes. The products were examined in a 300 kV JEOL JEM-3000F field emission gun HRTEM (C_s = 0.6 mm). Images were acquired on a Gatan model with Si [110] lattice spacings. Electron energy loss (EEL) (794 1 k CCD camera for which the magnification was calibrated) spectra were recorded with a Gatan image filter equipped with a 2 k 794IF/20 MegaScan CCD located below the 3000F column. Image simulations were performed with a standard multi-slice algorithm employing representative parameters for the 3000F.

The presence of *o*-carborane within SWNT bundles and individual SWNTs was confirmed by complimentary EELS studies, and HRTEM imaging and simulation (Fig. 2). It proved difficult to obtain reliable EELS spectra from individual filled SWNTs as these damaged rapidly when exposed to a focused 1 nm electron probe. Spectra were instead recorded from SWNT bundles with a spread beam (Fig. 2(a)) and clearly demonstrated the presence of B in the composite material (Fig. 2(b)). HRTEM images indicated the presence of discrete molecules (Fig. 2(c) and (d)) and short chains of *o*-carborane within SWNTs (Fig. 2(g) and (h)). Where single molecules were observed, it was reasonable to conclude that these are located inside the SWNTs, as indicated in Fig. 2(e), as *o*-carborane material located on the outside of the SWNTs rapidly vaporized in the electron beam whereas discrete molecules remain 'fixed' inside the tubule upon continued exposure to the electron beam for 1–2 min. The observed imaging behaviour of these molecules was also consistent with computer image simulations (Figs. 1(c) and 2(f)). In the case of short chains formed inside moderately wide (*i.e.* 1.4–1.6 nm diameter) SWNTs (Figs. 2(g) and (h)), these invariably formed 'zig-zag' chains (*i.e.* rather than linear chains as reported for C_n@SWNTs[2]) as represented schematically in Fig. 2(i). We assume that this packing behaviour results from clusters of molecules being compressed into these staggered arrangements by the van der Waals surface of the encapsulating SWNT.

The *o*-carborane molecules within the 'zig-zag' chains apparently packed somewhat closer (*i.e.* 0.5–0.6 nm) than the 'nearest neighbour' distance of ~0.7 nm predicted from the bulk structure model.[10] Additionally, this packing behaviour

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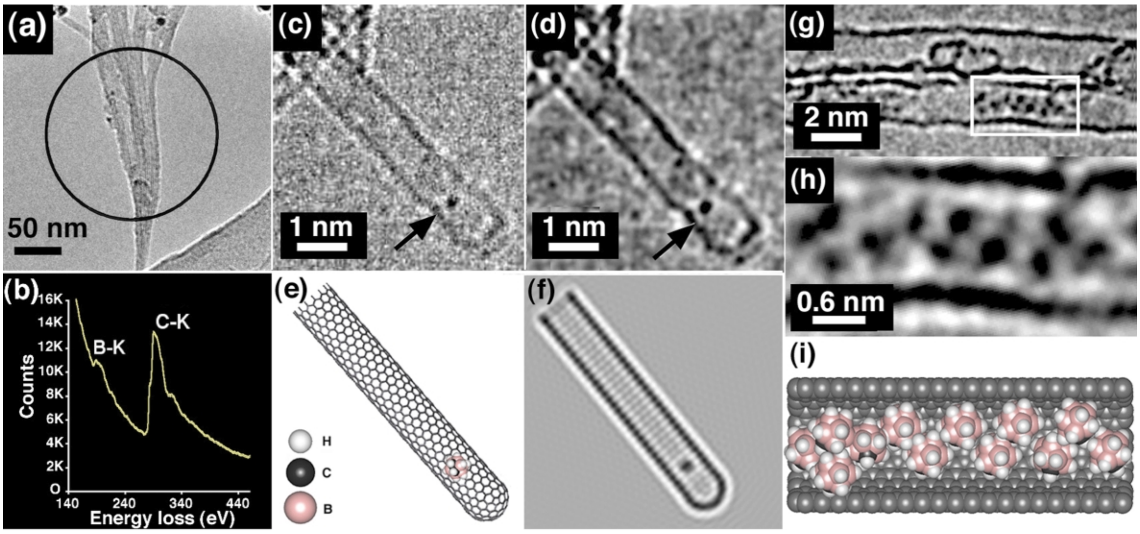

Fig. 2 (a) Low magnification HRTEM image of several bundles of SWNTs treated with *o*-carborane. (b) EELS spectrum obtained from indicated region in (a). (c) and (d) HRTEM image and noise-filtered image of a discrete *o*-carborane molecule within the tip of a capped 1.2 nm diameter SWNT. (e) and (f) structure model and Scherzer focus simulation a single *o*-carborane molecule within a SWNT tip. (g) and (h) HRTEM image and detail obtained from a short chain of *o*-carborane molecules formed within a ~1.6 nm diameter SWNT. (i) Schematic representation of nanostructure in (h).

differs markedly from that typically observed for fullerene and endofullerene molecules encapsulated within similar diameter SWNTs which typically form linear chains in which individual molecules are separated by slightly less than the predicted van der Waals separation of ~0.34 nm due to van der Waals compression by the SWNT.[13] The shortening of the intermolecular distances can be attributed partially to the packing behaviour as the molecules will stagger in projection with the result that the observed separation will seem less in a two-dimensional image. Additionally, van der Waals compression effects may also contribute to a shortening of the observed spacing by analogy with ref. 13. The observation of ‘zig-zag’ rather than linear chains can be directly attributed to the smaller size of the *o*-carborane molecules compared to C_{60} (Fig. 1(a) and (b)). The latter fit relatively snugly inside narrower (*i.e.* 1.2 and 1.6 nm) SWNTs whereas the smaller *o*-carborane molecules can more readily compress into staggered arrays (*i.e.* Figs. 2(h) and (i)).

Estimated filling yields for these experiments were quite low, varying from 5–20%, and were somewhat sensitive to the processing of the SWNT sample used. The highest yields came from using acid treated SWNTs although SWNT samples pre-treated, by heating in 20% O_2 at 420 °C for 20 minutes, showed no improvements to filling yields, contrary to reports that this drastically increases the filling yields of fullerene encapsulation for acid treated PLV SWNTs.[3] This could possibly be due to the sensitivity of purification and opening treatments to the type of SWNT material, as the samples were prepared using arc-synthesised SWNTs.

It has been shown that successful encapsulation of *o*-carborane into SWNTs has been achieved, using a sublimation technique, thus performing the first introduction of a boron containing species into carbon nanotubes and the only ′spherical′ molecules, other than fullerenes, to be observed packing in them. This encapsulation is confirmed both by HRTEM and EELS observations. There has been one report of the encapsulation of boron carbide with multi-walled graphitic layers,[14] but there have been no reported cases of filling carbon SWNTs with boron containing species. The resulting composites represent the first example of non-fullerenic spheroidal molecules forming ‘peapod’ (where the ‘peas’ are effectively ‘petit pois’ due to their smaller size compared to conventional fullerenes) -type structures.

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