CHEMCOMM
Communication
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Electron beam induced *in situ* clusterisation of 1D $ZrCl_4$ chains within single-walled carbon nanotubes

Gareth Brown,[ab] Sam R. Bailey,[a] Jeremy Sloan,[ab] Cigang Xu,[a] Steffi Friedrichs,[a] Emmanuel Flahaut,[a] Karl S. Coleman,[a] John L. Hutchison,[b] Rafal E. Dunin-Borkowski[b] and Malcolm L. H. Green*[a]

[a] *Wolfson Catalysis Centre (Carbon Nanotechnology Group), Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: malcolm.green@chem.ox.ac.uk*
[b] *Department of Materials, University of Oxford, South Parks Road, Oxford, UK OX1 3PH*

Received (in Cambridge, UK) 8th February 2001, Accepted 7th March 2001
First published as an Advance Article on the web 17th April 2001

Cluster formation can be induced *in situ* in SWNTs filled with $ZrCl_4$ by electron beam irradiation of SWNT/$ZrCl_4$ composites within a field emission gun transmission electron microscope (FEGTEM); the process represents a possible route to the synthesis of 1D-quantum dot arrays formed by related materials.

Single-walled carbon nanotubes (SWNTs)[1] can be filled by solution-deposition[2] or capillarity methods[3] similar to those used to fill multi-walled carbon nanotubes (MWNTs).[4,5] There is now considerable theoretical[6,7] and experimental[8–11] evidence indicating that doped SWNTs show enhanced conductive or opto-electronic properties compared to untreated tubules. In addition, as most SWNTs fall within a narrow 1.2–1.6 nm diameter range when formed by vaporisation of catalytically doped carbon,[12,13] their capillaries can template the formation of atomically thin crystals of tubule-specified diameters. Recently these have included 2×2 and 3×3 atomic layer thick KI crystals,[14,15] helical iodine chains,[9] 1D polyhedral chains of lanthanide halide crystals[16] and chains of fullerene or endo-fullerene molecules.[17–20] In this study, we show how discrete $ZrCl_x$ (with $0 \leqslant x < 4$) clusters of constrained diameters can be formed within SWNTs by electron-beam irradiation of tubules filled with $ZrCl_4$.

The SWNTs used in this work were prepared by a catalytic arc synthesis method.[13] $ZrCl_4$ was resublimed at 693 K under N_2 from the as-supplied product (Aldrich, 99.9%). As-prepared SWNT material was mixed with $ZrCl_4$ in a 1:1 ratio by mass under dry box conditions and ground thoroughly. Each sample was sealed under vacuum in a silica glass ampoule and heated at 2 K min^{-1} to 623 K in a tube furnace, held at that temperature for 1 h and then furnace cooled to room temperature. The specimen was characterised in a JEOL 3000F FEGTEM operated at 300 kV and equipped with a Gatan 794 (1 k × 1 k pixel) CCD camera. The beam density in imaging mode was *ca.* 5×10^5 $e^- nm^{-2} s^{-1}$ which is equivalent to a current of *ca.*2.7×10^{-14} A. The chemical identity of the specimen was confirmed by energy-dispersive X-ray microanalysis (EDX) using a 0.5 nm diameter focussed electron probe, a LINK 'Pentafet' detector and an Oxford Instruments 'ISIS' 300 system.

When examined under the FEGTEM, both nanotube bundles and discrete SWNTs were observed to be filled continuously with 1D chains of $ZrCl_4$. EDX microanalysis performed on discrete filled SWNTs confirmed the chemical identity of the filling material. As a spread electron beam of specified electron density (see above) was held upon regions of filled SWNTs, the filling material underwent progressive changes in morphology as it segregated to form discrete clusters. The sequence of events was followed over periods of up to 20 min, after which the encapsulating SWNTs denatured.

Fig. 1 shows a sequence of ten FEGTEM images obtained over *ca.* 4 min. In the initial image **I**, two continuously filled SWNTs can be seen with the upper tubule being terminated by a cap visible on the right of the image. By image **II**, the filling in the bottom tubule has already segregated into three *ca.* 3–4 nm long clusters. By image **V**, the arrowed clusters have different lengths of 3, 2 and 4 nm, respectively. By image **VI**, the material in the topmost tubule had also segregated into two clusters (arrowed). By the final image **X**, discrete *ca.* 1 nm long clusters can be seen in the two nanotubes with the number of clusters in the bottom tubule increased from three (see image **V**) to four. It is important to note that during these initial transformations (*i.e.* before the denaturing of the SWNTs) the walls of the tubules remained relatively unchanged, indicating that no chemical interaction between the carbon walls and the filling material had occurred. A minimum length of *ca.* 1 nm for the clusters was eventually obtained after irradiation for *ca.* 8 min.

The microstructure of the filling material in image **I** is indistinct whereas several of the longer clusters in images **II**, **III** and **V** consist of 1D arrays of dark spots similar to those reported recently for lanthanide halides of the form $LnCl_3$ (Ln = La, Nd, Sm, Eu, Gd, Tb, Yb) formed within SWNTs.[16] In those structures, the dark spot arrays were attributed to 1D chains of edge-sharing $LnCl_6$ polyhedra, with the heavy Ln^{3+} cations dominating the image contrast over the less strongly scattering

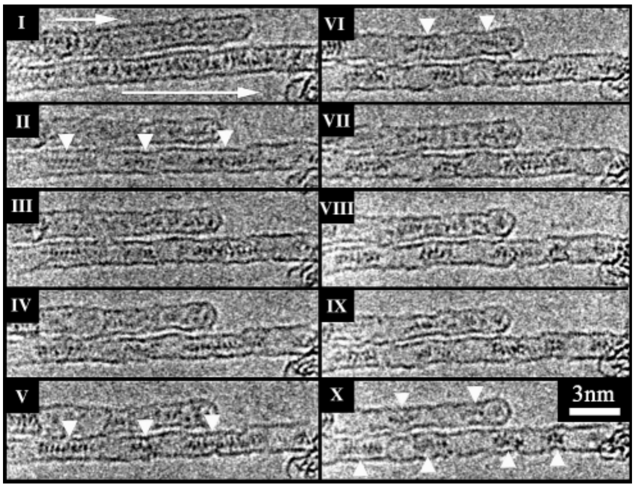

Fig. 1 Sequence of images **I** to **X** obtained at *ca.* 20 s intervals showing gradual clusterisation of $ZrCl_4$ within SWNTs induced by electron-beam irradiation within a FEGTEM. Image **I** shows two SWNTs continuously filled with $ZrCl_4$ (large arrows). After *ca.* 80 s (image **V**), filling in the bottom tubule has reformed into three distinct separated clusters (small arrows). After *ca.* 100 s (image **VI**) filling in the top tubule has segregated into two clusters. After 4 min (image **X**), the filling has segregated into a total of six distinct clusters (small arrows). In images **II**, **III** and **V**, distinct 1D arrays of dark spots are visible. Note 'bulging' either side of the central cluster in the lower SWNT in images **VI** and **VII**.

DOI: 10.1039/b101261o

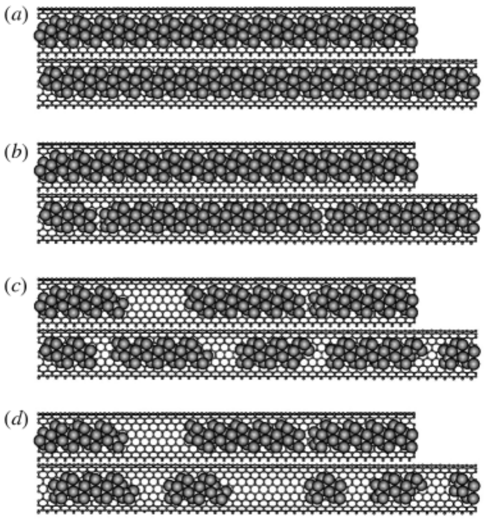

Fig. 2 Idealised structural representation of cluster formation within a pair of SWNTs. SWNTs continuously filled with $ZrCl_4$ (*a*) undergo beam irradiation until a break occurs in the filling after *ca.* 4–10 s (*b*). Either side of the break, the chains will terminate in reduced polyhedra. After 40–50 s, several long clusters are formed (*c*) and beam reduction continues until complete clusterisation occurs (*d*). This process may continue until all the chlorine is eliminated from the clusters.

Cl^- anions. It is therefore reasonable to assume that $ZrCl_4$, which forms an edge-sharing '*trans*' octahedral chain structure in the bulk,[21] forms similar 1D chains within SWNT capillaries and that the dark spots visible in images **I–X** in Fig. 1 correspond to more strongly scattering Zr^{4+} ions rather than to the weaker scattering Cl^- ions.

An additional interesting point is that the SWNTs distort during the clusterisation process. For example, in images **VI** and **VII** (Fig. 1) the lower tubule, which has a constant diameter of *ca.* 1.4 nm in the initial image (*i.e.* image **I**, Fig. 1), shows symmetric 0.1 nm 'bulges' either side of the central $ZrCl_x$ cluster. We believe that these 'bulges' are caused by complimentary ovaloid distortions in the SWNTs resulting from asymmetric distortions induced in the $ZrCl_x$ clusters by the beam rearrangement process. Such distortions will cause an apparent local variation in the SWNT diameter when viewed in projection in a FEGTEM.

Electron beam bombardment of MX_n halides at intermediate accelerating voltages (typically 100–400 kV) produces isolated stoichiometric Frenkel-type defects in bulk crystals.[22,23] However, in smaller volume halide crystallites (*ca.* 1 μm^3 particle size) elimination of halogen and the formation of surface metal occurs instead.[24] We propose therefore that the 1D $ZrCl_4$ chains undergo sequential elimination of chlorine to form clusters of $ZrCl_x$, of progressively lower stoichiometry (*i.e.* x decreases from 4 to 0), according to the schematic depiction in Fig. 2(*a*)–(*d*). Complete elimination of chlorine would result in the formation of metallic Zr clusters although we have not yet been able to verify this. Similarly, it has not been possible to determine the nature of the eliminated chlorine species (*i.e.* such as radicals, ions, charged molecular fragments, *etc.*). We assume that chlorine diffuses out of side-wall defects or open ends of SWNTs in the same way that gaseous endofullerene molecules have been demonstrated to diffuse into them.[19,20] As no significant damage to the SWNT walls was observed during clusterisation, carburisation of the clusters is not thought to occur, although surface reaction of the carbon with the eliminated chlorine species (see above) remains a possibility.

In conclusion, $ZrCl_4$ contained within SWNTs can be beam-reduced *in situ* to form $ZrCl_x$ clusters (with $0 \leqslant x < 4$) of controlled diameter. While beam-induced coalescence of fullerene molecules has been reported within SWNTs,[17,18] this is the first time that cluster segregation has been reported. If this phenomenon can be extended in a controlled way to bulk SWNT samples containing semiconducting or metallic species (or their precursors) then this may represent a route to the synthesis of one dimensional arrays of quantum dots within SWNTs. In addition, more detailed analytical studies of the clusterisation phenomena (*e.g.* high resolution EELS studies[20]) should lead to a better understanding of the mechanism of halide decomposition for these virtually 'all surface' crystals.

Financial support was provided by Petroleum Research Fund, administered by the American Chemical Society (grant No. 33765-AC5), the EPSRC (grant nos. GR/L59238 and GR/L22324) and Colebrand Ltd. for financial support. C. X. is grateful for a K. C. Wong Scholarship (University of Oxford), a Light Senior Scholarship (St Catherine's College, Oxford) and the Henry Lester trust. S. F. is indebted to BMBF and to the Fonds der Chemischen Industrie for additional financial support. J. S. and K. S. C. are indebted to the Royal Society.

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