COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Single-walled carbon nanotubes filled with *M* OH (*M* = K, Cs) and then washed and refilled with clusters and molecules

Narun Thamavaranukup,[a] Henning A. Höppe,[a] Luisa Ruiz-Gonzalez,[a] Pedro M. F. J. Costa,[a] Jeremy Sloan,*[ab] Angus Kirkland*[ab] and Malcolm L. H. Green*[a]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR.*
E-mail: jeremy.sloan@chem.ox.ac.uk; malcolm.green@chem.ox.ac.uk; Fax: +44-(0)1865-272690;
Tel: +44-(0)1865-272645

[b] *Department of Materials, University of Oxford, Parks Road, Oxford, UK OX1 3PH.*
E-mail: angus.kirkland@materials.ox.ac.uk; Fax: +44-(0)1865-283333; Tel: +44-(0)1865-273662

Received (in Cambridge, UK) 21st April 2004, Accepted 8th June 2004
First published as an Advance Article on the web 28th June 2004

Heating single-walled carbon nanotubes (SWNTs) with molten hydroxides *M*OH (*M* = K, Cs) gave *M*OH@SWNT in good yield; high resolution transmission electron microscopy (HRTEM) indicated that CsOH in CsOH@SWNT often adopts twisted 1D crystal structures inside SWNTs; treating *M*OH@SWNT with water at room temperature removes the soluble hydroxide filling and the resulting SWNTs may then be filled using aqueous solutions of uranyl acetate or uranyl nitrate at rt giving SWNTs filled with UO_2 clusters and uranyl acetate molecules.

Multi-walled carbon nanotubes (MWNTs)[1] have been filled with many materials and frequently the filling can be effected by addition of solutions to MWNTs which have been previously opened using oxidising agents such as nitric acid or gas phase oxidants to selectively open the nanotube tips.[1–3] In many cases the filling materials can be removed by treating the SWNTS with a suitable solvent.[2] Indeed selective removal of material from the exterior of such filled MWNTs cannot be readily achieved and special methods, for example, inverse micelles have been employed as washing agents.[4] In contrast, many filled SWNT samples retain their filling material despite vigorous attempts to remove the filling. For example, samples of KI@SWNT remain unchanged after being refluxed in water in a Soxhlet apparatus for three days or washing in cold water for 90 days.[5] Here we report the high yield filling of SWNTs with the hydroxides *M*OH, (*M* = K, Cs), and the facile removal of the *M*OH filling by treatment with water. Following this treatment, the SWNTs could then be refilled with UO_2 clusters or discrete molecules of uranyl acetate under mild conditions.

As-made arc SWNTs[6] (0.010 g) were heated with CsOH (0.025 g, Sigma Aldrich, 99.97%) in a sealed silica ampoule to 573 K at a rate of 3 K min^{-1}, maintained at this temperature for 4 h and then allowed to slowly cool to room temperature (3 K min^{-1}). KOH@SWNTs (0.025 g, Fluka, 99.9%) were prepared similarly; they were heated at a rate of 3 K min^{-1} to 723 K, maintained at this temperature for 4 h and then allowed to slowly cool to room temperature (1 K min^{-1}). The samples were then examined by HRTEM.† The SWNTs treated with CsOH were found to be partially coated with non-crystalline material but were also filled in *ca.* 20–30% yield with either crystalline (Fig. 1(a)) or partially crystalline hydroxide. There was also some evidence for interstitial filling in SWNT bundles treated with CsOH. In the case of the KOH sample, the contrast afforded by the low atomic number of K made the identification of this material by HRTEM difficult however, energy dispersive X-ray microanalyses (EDX) confirmed the presence of Cs and K in the CsOH@SWNT and KOH@SWNT samples, respectively.

Bulk CsOH exhibits an orthorhombic polymorph with an *anti*-NaOH type structure stable to 497.5 K and a cubic phase isotypic with NaCl above this temperature.[1] Fig. 1(b) shows a noise filtered HRTEM image in which the microstructure of the CsOH filling is visible as a crystalline arrangement of dark spots with the image contrast being dominated by the heavy Cs atom columns. Two different regions are observed denoted I and II in Fig. 1(b). In region I the columns order into a hexagonal array that cannot be reconciled with orthorhombic CsOH but more closely resembles a fragment derived from the monohydrate (*i.e.* $CsOH(H_2O)$ space group *P*6/*mmm*, no. 191).[7] In region II the microstructure changes into pairs of linear atom columns similar to those observed in KI@SWNT.[5] Additionally, the diameter of the SWNT varies from 1.3 nm (region I) to 1.2 nm (region II). The distortion of the crystal might be attributed to twinning or to the coexistence of two hydrate phases inside the SWNT. Image simulations performed using a model formed from a distorted section of SWNT and two fragments of a bilayer of $CsOH(H_2O)$ rotated by 90° (*i.e.* Fig. 1(c)) produced a good agreement with the experimental image (*cf.* Figs. 1 (b) and (d)). The hexagonal (I) and columnar patterns (II) can therefore be transformed into each other by rotating the encapsulated nanocrystal by 90°.

The section of crystal in region I is disordered and the Cs–Cs distances measured parallel to the tube axis ranged from 0.32 nm to 0.42 nm (average 0.36 nm) and, measured diagonally with respect to the tube axis, averaged 0.40 nm. In bulk $CsOH(H_2O)$ the equivalent Cs–Cs distance is 0.458 nm.[1] The apparent contraction of the Cs–Cs distances inside the SWNT may reflect the lower coordination number of the surface Cs atoms.

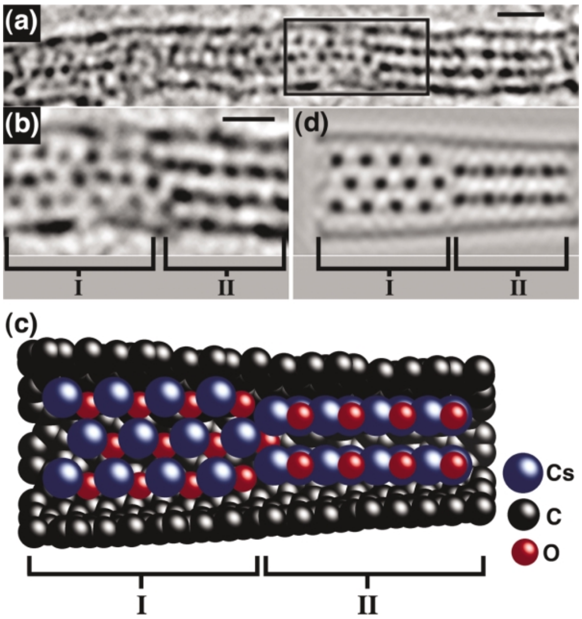

Fig. 1 (a) TEM image of CsOH@SWNT (scale bar = 1.0 nm). (b) Enlarged TEM image of CsOH@SWNT (scale bar = 0.6 nm). (c) Schematic representation of the twinning transforming zone I into II. (d) Scherzer defocus simulated TEM image based on (c).

DOI: 10.1039/b405956e

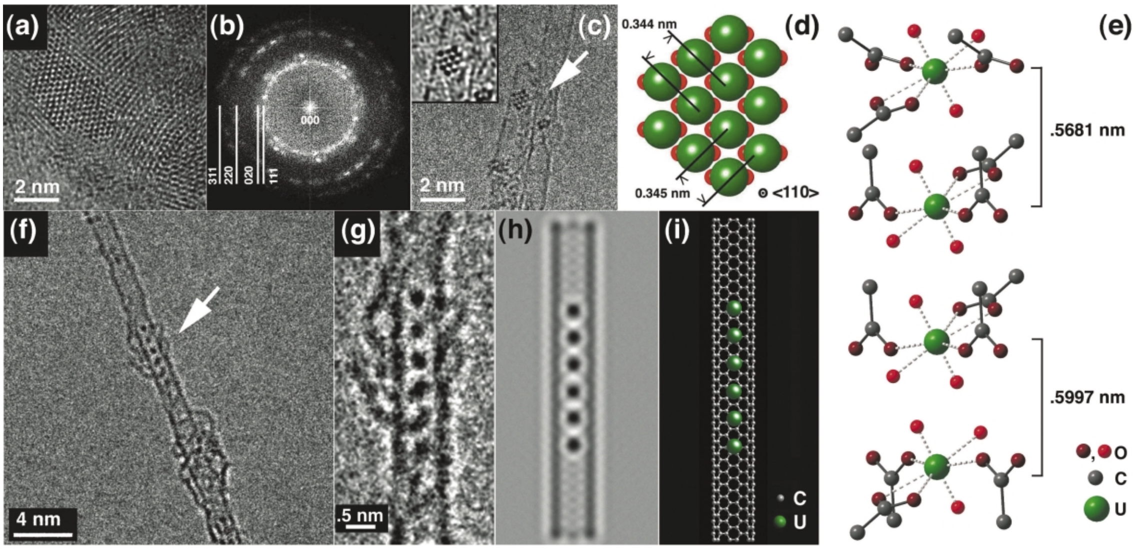

Fig. 2 (a) TEM image of polycrystalline UO_2 outside SWNTs. (b) FFT of (a). (c) TEM image and detail of UO_2 clusters inside SWNTs. (d) Structure model of the encapsulated UO_2 cluster in (c). (e) Schematic representations of the crystal structure of uranyl acetate showing the two shortest U–U distances (top and bottom, H atoms omitted). (f) TEM image of molecular uranyl acetate inside SWNTs. (g) Detail from indicated region in (f). (h) Simulated TEM image (i) Structure model of uranyl acetate–SWNT composite used in simulation (O atoms and acetate groups omitted for clarity).

When the *M*OH@SWNT samples were rinsed with water, exhaustive EDX analyses confirmed that all Cs^+ and K^+ ions, corresponding to the respective hydroxides, had been removed.‡ The post-washed SWNTs were then treated with aqueous uranyl nitrate or uranyl acetate.§ HRTEM images of these samples revealed the presence of a polycrystalline material outside the SWNTs in both cases displaying a similar microstructure to that shown in Fig 2(a). The *d* values obtained by a Fast Fourier Transform (FFT) of this example (Fig. 2(b); 0.313 nm, 0.280 nm, 0.195 nm and 0.165 nm) fit well with respective *d*-spacings of the {111}, {200}, {220} and {311} planes in bulk UO_2.[8] In *ca.* 25% of the larger diameter tubes (> 1 nm) we observed in both cases similar clusters to the example shown in Fig. 2(c). This cluster corresponds to a small fragment of UO_2 derived from a $\langle 110 \rangle$ projection of the bulk phase with the 0.34 nm {111} lattice planes being clearly visible in the enlarged detail inset in Fig. 2(c). The structure of this cluster is reproduced schematically in Fig. 2(d). A few narrow diameter SWNTs (*i.e.* < 1 nm) of the post-washed SWNTs treated with uranyl acetate (structure Fig 2(e)),[9] exhibited linear rows of dark dots (*e.g.* Fig. 2(f)) instead of UO_2 consistent with the encapsulation of discrete molecules of the acetate. The dark spots correspond to the strongly scattering U cations in uranyl acetate and indicate the presence of stacked molecules inside the SWNTs (*cf.* Fig. 2(e)). The shortest U–U distances found in bulk uranyl acetate[9] are 0.568 nm and correspond well with the measured U–U distances in this image of 0.55 nm. The good agreement between experimental and simulated images based on this structural model is obvious (Figs. 2(h) and (i)) although only the positions of the strongly scattering U atoms is clear. The relative dispositions of the acetate functional groups within the SWNT is currently unknown but these presumably act as steric spacers within the tubule that permit the strongly scattering U atoms to be imaged discretely. Also this microstructure clearly cannot be reconciled with UO_2. The diameter of the tube in Fig 2(f) is 0.90 nm (*i.e.* a (1,11) SWNT) and there is just enough space for a single row of uranyl acetate molecules inside this tube. In larger SWNTs, decomposition of uranyl acetate to UO_2 clusters was observed. Other examples of discrete molecules encapsulated in SWNTs are chains of C_{60} and *o*-carboranes.[10] Yudasaka *et al.* have also reported the facile insertion of fullerenes and endofullerenes in SWNTs oxidised at 520 °C.[11]

We acknowledge support to H. A. H. from the Postdoctoral-Programme of the German Academic Exchange Service (DAAD). L. R.-G. thanks the European Union for support *via* the NANO-TEMP Research Training Network.

Notes and references

† Samples of each step were dispersed in $CHCl_3$ and placed dropwise onto a holey carbon support grid and examined in a JEOL JEM-3000F HRTEM (point resolution 0.16 nm) equipped with an ISIS 300 system (Oxford Instruments) equipped with a LINK "Pentafet" EDX detector. High resolution images were acquired digitally using GATAN 794 (1 k × 1 k pixel) CCD cameras.

‡ Two portions of the obtained samples were washed by stirring in 50 ml of deionised water, one at room temperature for 30 min whereas the second one was stirred at 373 K for 5 h. After filtering both samples were dried at 473 K for 24 h. We refer to these samples as post-washed.

§ Uranium salts were incorporated into post-washed SWNTs by stirring in saturated solutions of uranyl acetate (343 K) and uranyl nitrate (rt), respectively, for 48 h. Additional blank experiments reacting as-made SWNTs with uranyl acetate in the same conditions failed to fill uranium salts into as-made SWNTs.

1 S. Iijima, *Nature*, 1991, **345**, 56.
2 S. C Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, *Nature*, 1994, **372**, 160.
3 P. M. Ajayan and S. Iijima, *Nature*, 1993, **361**, 333; P. M. Ajayan, T. W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki and H. Hiura, *Nature*, 1993, **362**, 522.
4 J. Cook, J. Sloan, R. J. R. Heesom, J. Hammer and M. L. H. Green, *Chem. Commun.*, 1996, (23), 2673.
5 G. Brown, S. R. Bailey, M. Novotny, R. Carter, E. Flahaut, K. S. Coleman, J. L. Hutchison, M. L. H. Green and J. Sloan, *Appl. Phys. A*, 2003, **76**, 1.
6 C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapells, S. Lefrant, P. Deniard, R. Lee and J. E. Fischer, *Nature*, 1997, **388**, 756.
7 H. Jacobs and B. Harbrecht, *Z. Naturforsch.*, 1981, **36b**, 270; J. W. Otto and W. B. Holzapfel, *J. Phys. Condens. Matter*, 1995, **7**, 5461; N. Acquista, S. Abramowitz and D. R. Lide, *J. Chem. Phys.*, 1968, **49**, 780; H. Jacobs and B. Harbrecht, *Z. Anorg. Allg. Chem.*, 1982, **491**, 154.
8 F. Hund, *Z. Anorg. Allg. Chem.*, 1964, **333**, 248.
9 J. Howatson, D. M. Grev and B. Morosin, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1933.
10 B. W. Smith, M. Monthioux, D. E. Luzzi and J. E. Fischer, *Nature*, 1998, **296**, 323; D. A. Morgan, J. Sloan and M. L. H. Green, *Chem. Commun.*, 2002, **20**, 2442.
11 M. Yudasaka, K. Ajima, K. Suenaga, T. Ichihashi, A. Hashimoto and S. Iijima, *Chem. Phys. Lett.*, 2003, **380**, 42.