Synthesis of carbon nanotubes containing metal oxides and metals of the d-block and f-block transition metals and related studies

Y. K. Chen, A. Chu, J. Cook, M. L. H. Green, P. J. F. Harris,† R. Heesom, M. Humphries, J. Sloan, S. C. Tsang† and J. F. C. Turner‡

Inorganic Chemistry Laboratory, University of Oxford, Oxford, UK OX1 3QR

The filling of carbon nanotubes with metals and metal oxides *via* one- and two-step processes is presented. Both molten media and wet chemistry solution methods have been used to introduce foreign materials into the hollow nanotube cavities. Chemical reactions inside the tubes have been carried out, including the reduction of encapsulated materials to the metals. The nature of the crystalline filling has been found to be highly dependent on the techniques used. Wet chemical methods tend to result in filling which consists of discrete crystallites, whereas molten media methods tend to give long, continuous single crystals.

The macroscopic synthesis of carbon nanotubes by the arc vaporization of graphite was first reported by Ebbesen and Ajayan in 1992.[1] The tubes which are formed consist of 2–20 multilayers of graphene sheets that are arranged concentrically in a 'Russian doll' manner.[2] Typically, they have hollow internal cavities with diameters of 3–10 nm and are 100–500 nm in length.

Nanotubes prepared by the arc-vaporization method are closed at both ends. It has been shown that these caps may be removed, leading to the filling of the inner cavity with metals,[3] metal oxides[3–5] and even biomolecules such as cytochrome c.[6,7] The first example of opened and filled nanotubes was reported by Ajayan and Iijima, who showed that the treatment of closed tubes with lead in the presence of air, leads to filling with continuous regions of metal oxide material.[4,5] The tube ends can also be removed in a selective oxidation process using carbon dioxide[8] or oxygen,[9] although both methods give poor yields of opened nanotubes and cause damage to the graphitic walls. Recently, we have shown that the treatment of closed tubes with refluxing nitric acid gives very high yields of opened tubes and does not etch the tube walls.[3] When this reaction is carried out in the presence of a metal nitrate, after annealing at *ca.* 400 °C, many of the opened tubes are found to contain discrete crystals of the metal oxides.

Carbon nanoparticles filled with metal materials have also been formed *via* an *in situ* synthesis, involving the arc evaporation of composite carbon electrodes made by blending graphite powder with metals or metal oxides.[10–14] The resulting materials have closed carbon shells with the encapsulated materials being either the pure metals or metal carbides. This method can also give nanotubes filled with crystalline materials which, depending on the conditions and the metal in question, vary from continuous crystals that fill the entire hollow cavity to discrete crystals which are positioned in different locations along the length of the tube.[15]

In this work, we describe the preparation and characterization of carbon nanotubes containing a wide range of metal oxides, elemental metals and related materials. Preliminary reports of parts of this work have been published elsewhere.[3,16–18]

Experimental

Production of carbon nanotubes

Carbon nanotubes were prepared from *ca.* 1 cm diameter graphite rods by the standard modified arc-discharge method in 0.13 atm of helium using a dc voltage of 30 V and a current of *ca.* 180 A.[8]

Typical preparation for the one-step filling method

A round-bottomed flask containing a sample of closed nanotubes (0.5 g), azeotropic nitric acid (68%; *ca.* 100 ml) and the soluble metal nitrate (*ca.* 0.5–1 g) was heated to reflux for 4.5–12 h. The nitric acid solution was decanted off, and the black sludge was pipetted onto glass filter paper. The sample was dried overnight in an oven at 60 °C, and then calcined by heating in a stream of argon at 450 °C for 5 h for conversion of the nitrate to the corresponding metal oxide. Reduction to the metal, where possible, was carried out in a similar manner, usually by heating to 500 °C under a continuous stream of H_2.

Typical preparation for the two-step filling method

The nanotubes were opened by oxidation with azeotropic HNO_3 at 11 °C for 8–24 h.[3] The tubes were then filtered onto glass filter paper, washed copiously with deionized water and then dried in the air in an oven overnight at 160 °C. This method of opening nanotubes results in the formation of acid functionalities (CO_2H, OH) on the surfaces of nanotubes.[18] Heating nanotubes slowly to 900 °C results in the removal of these acidic groups, as shown by the loss of CO_2 and CO from the samples. This pre-treatment is also used when the material which is desired to fill the nanotubes is sensitive to oxygen groups (*i.e.* UCl_4, as described below).

Two-step method with metal complexes

A sample of opened carbon nanotubes (250 mg) was added to a solution of a metal complex (*ca.* 1 g) dissolved in a minimal volume of solvent (*ca.* 5 ml). This procedure may be carried out for air-sensitive materials, using organic or aqueous solvents. The mixture was then stirred overnight and the excess solution decanted off. The resulting black sludge was pipetted onto glass filter paper and dried in an oven overnight at 60 °C. Calcination of the materials was carried out as described for the one-step procedure.

---

† Present address: The Catalysis Research Centre, Department of Chemistry, University of Reading, Whiteknights, Reading, UK RG6 6AD.

‡ Present address: Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, DE 19711, USA.

Typical preparation for the molten media method

A sample of opened carbon nanotubes (*ca.* 0.5 g) was ground in a mortar and pestle with the inorganic material (*ca.* 0.5 g). The nanotubes used with air-sensitive halides, such as $ZrCl_4$, were decarboxylated prior to use.[18] The mixture was placed in a silica ampoule and evacuated under high vacuum for 2 h before sealing. The ampoule was placed in a temperature-programmed furnace, and then heated from room temperature to the desired temperature at a heating rate of $10\,^{\circ}C\ min^{-1}$. The ampoule was kept at that temperature for 1–8 h and allowed to cool slowly to room temperature at a rate of $1\,^{\circ}C\ min^{-1}$. Air-sensitive samples were oxidized after heating by opening the ampoule to air and allowing contact with oxygen and water.

Methods of characterization

The samples were dispersed in CH_2Cl_2 and sonicated for 5 min before being deposited onto a lacey carbon film. High-resolution transmission electron microscopy (HRTEM) was performed using JEOL 4000EX, JEM 2010F and JEOL 2000EX microscopes operated at optimum defocus with accelerating voltages of 400, 200 and 200 kV, respectively. Lattice spacings on encapsulated crystals were calculated using the 3.4 Å separation in the graphite layers of the nanotubes as an internal standard. The overall yields of filled nanotubes were estimated by the visual inspection of portions of the sample using HRTEM. EDS was performed on the JEOL 2010F microscope operating at 200 kV using the smallest available probe (0.7 nm). A Philips PW1710 diffractometer with Cu-Kα_1 radiation operating in the θ–2θ mode was used for the XRD measurements which were obtained on all samples. The data was then compared to known literature spectra obtained from the Powder Diffraction Data File (JCPDF).

Results and Discussion

One-step method

This treatment results in the encapsulation of the metal nitrate inside nanotubes and its conversion to the crystalline oxide. Attempts to observe metal nitrates by HRTEM were inconclusive (*i.e.* without heat treatment) and revealed only amorphous material both inside and outside the nanotubes. If the calcination process is not carried out slowly ($<5\,^{\circ}C\ min^{-1}$), few filled nanotubes are observed. Presumably this results from the rapid expulsion of the solution molecules present in the nanotube cavities, causing the metal complex to be forced out of the tubes.

Examination of the specimens by HRTEM revealed that, in many cases, it was possible to obtain firm evidence for the identity of the encapsulated materials from the direct observation of lattice fringes of single crystals. Indeed, this technique proved to be more reliable in terms of characterizing the composition of the encapsulates than X-ray diffraction analysis, as the latter was capable of characterizing the bulk specimen only. The measured magnitudes of the layer separations were then compared with literature values. These results are summarized in Table 1.

Fig. 1(a)–(c) show HRTEM images of encapsulated oxide crystallites of NiO, Sm_2O_3 and Nd_2O_3. Carbon nanotubes containing oxides of the metals Co, Pd, Cd, Fe, Y, La, Ce, Pr, Nd, Eu and U[18] have also been prepared using this one-step method. It is interesting to note that in the case of the Nd_2O_3 filled tubes, insertion of amorphous and crystalline material between the carbon layers has occurred. This insertion causes the carbon layers to buckle, giving an interlayer separation of up to 20 Å, in contrast to the normally observed 3.4 Å separation. Similar insertion of amorphous materials has been observed previously when V_2O_5 was melted into carbon nanotubes and $AuCl_3$ encapsulated using the two-step method.

Extensive and detailed HRTEM studies showed that this method of filling carbon tubes gave samples in which there were also metal oxide crystals exterior to the tube cavities. These are formed from the traces of mother liquor left on the filter paper after collection. Attempts to remove this extraneous residue by washing, for example with water or dilute nitric acid, invariably led to the elution of the nitrates from the interiors of the tubes.

The TEM studies also showed that, with exception of PdO and UO_{2-x}, samples of the oxide crystallites appeared to fill the entire internal diameter of the nanotubes (*ca.* 3–6 nm). Most of these crystallites are in the form of elongated particles, typically ranging from 10 to 40 nm in length. Occasionally, ellipsoidal or spherical crystallites which are considerably

Table 1 HRTEM observed lattice spacings of encapsulated metals and metal oxides

encapsulated metals and metal oxides	starting materials	observed lattice spacing[a]/Å	correlating planes {*hkl*}	literature spacing/Å
La_2O_3	$La(NO_3)_3{\cdot}6H_2O$	2.8, 3.5	{−303}, {202}	2.799, 3.59
Pr_2O_3	$Pr(NO_3)_3{\cdot}6H_2O$	2.8, 3.1, 3.5, 4.1	{012}, {302}, {400}, {102}	2.875, 3.15, 3.55, 4.17
CeO_2	$Ce(NO_3)_3{\cdot}6H_2O$	3.08	{111}	3.123
Y_2O_3	$Y(NO_3)_3{\cdot}5H_2O$	2.65	{400}	2.652
Nd_2O_3	$Nd(NO_3)_3{\cdot}xH_2O$	3.01	{002}	2.998
Sm_2O_3	$Sm(NO_3)_3{\cdot}6H_2O$	3.21	{222}	3.155
$FeBiO_3$	$Fe(NO_3)_3{\cdot}9H_2O+Bi(NO_3)_3{\cdot}5H_2O$	2.8, 3.9	{110} or {−110}, {100}	2.811 or 2.783, 3.95
UO_{2-x}	$UO_2(NO_3)_2{\cdot}6HO$	3.15	{111}	stoichiometry varies
NiO	$Ni(NO_3)_2{\cdot}6H_2O$	2.40	{111}	2.41
MoO_3	MoO_3	3.85	{110}	3.81
MoO_2	MoO_3	3.44, 2.47	{−111}, {111}	3.42, 2.43
ZrO_2	$ZrCl_4$	3.16, 2.89	{−111}, {1−11}	3.165, 2.84
ZrO_2	$ZrO(NO_3)_2{\cdot}xH_2O$	2.98	{111}	2.96
Re metal	$KReO_4$	2.30	{002}	2.226
Pd metal	$Pd(NO_3)_2$	2.26	{111}	2.245
Ag metal	$Ag(NO_3)$	2.40	{111}	2.359
AuCl	$AuCl_3$	5.32	{101}	5.33
Au metal	$AuCl_3$	2.325	{111}	2.355
CdO	$Cd(NO_3)_2{\cdot}4H_2O$	1.9, 2.6	{220}, {200}	1.877, 2.655
CdS	$CdO+H_2S$	2.5, 1.8, 1.7	{102}, {200}, {004}	2.450, 1.791, 1.679

[a] ±0.1 Å.

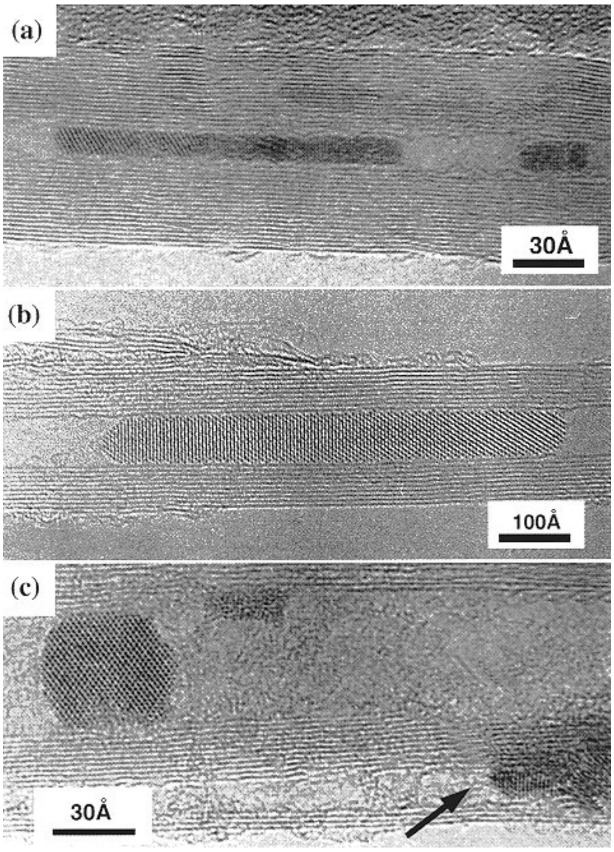

Fig. 1 (a) Nanotube filled with nickel material; the observed fringes of 2.4±0.05 Å correspond to the distance between the (111) planes in NiO. (b) Encapsulated single crystal of Sm_2O_3 with two sets of lattice fringes seen inside a carbon nanotube. The Sm_2O_3 lattice fringes 90° to the nanotube wall correspond to the (400) lattice planes of Sm_2O_3. (c) Nanotube containing cavity intercalated crystalline Nd_2O_3 (in the bore of the nanotube) and intralayer intercalated Nd_2O_3 (arrowed).

smaller than the cross-section of the inner diameter of the nanotube are observed, as was the case for PdO and UO_{2-x}.[3,18]

Stoichiometric mixed metal oxides were also be prepared using solutions containing the ions of two different metals. For example, refluxing closed nanotubes in a nitric acid solution containing equimolar amounts of $Fe(NO_3)_3\cdot 9H_2O$ and $Bi(NO_3)_3\cdot 5H_2O$ gave, after annealing, nanotubes filled with crystals of the mixed oxide, $FeBiO_3$ (Fig. 2). Attempts were also made to synthesize $NiCo_2O_4$, $LaCrO_3$, $MgCeO_3$, $LaFeO_3$, and $Nd_{1.85}Ce_{0.15}CuO_4$. It was found, however, that the formation of mixed oxides inside nanotubes *via* their mixed nitrate solutions was far from straightforward. For example, in the case of $Nd_{1.85}Ce_{0.15}CuO_4$, a definite assignment of the Nd and Ce stoichiometries of encapsulated crystallites could not be made, with the observed lattice fringes corresponding to $[Ln]CuO_4$, where $[Ln]=Nd_2$ or $Nd_{2-x}Ce_x$. It was also possible to identify large amounts of Nd_2O_3 located external to the nanotube cavities.

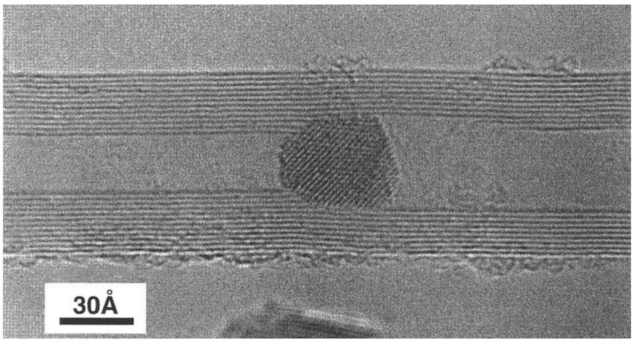

Fig. 2 A high-resolution electron micrograph of an encapsulated $FeBiO_3$ crystallite possessing a lattice with a 2.8 Å spacing. This distance corresponds to the inter-layer spacing between the (110) planes of $FeBiO_3$. The crystal appears to have grown where an internal cap is present, as the internal cavity changes diameter at this point.

The two-step method

This method has been useful for filling tubes with materials which are neither soluble nor stable in refluxing nitric acid. Carbon nanotubes filled with $H_4SiW_{12}O_{40}$ have been obtained by stirring the opened tubes with a concentrated solution of $H_4SiW_{12}O_{40}$ in deionized water for 16 h. Nanotubes filled with $RhCl_3$, $RuCl_3$, $PdCl_2$, $[NH_4]IrCl_6$, $[Ni(\eta\text{-}C_5H_5)_2]$ and $Co_2(CO)_8$ have also been prepared by this method. This two-step method normally gave lower percentage of filled tubes (*ca.* 20–30%) than the one-step *in situ* method.

As described previously, when the two-step method was used to encapsulate $AuCl_3$ or $AgNO_3$, an unusually high percentage of opened nanotubes were filled with the gold chloride or silver nitrate, respectively (*ca.* 70%).[16] In the case of gold, most of the encapsulated material consisted of spherical crystallites of the metal, ranging from 10 to 50 Å in diameter. Also present were crystallites of AuCl, which resulted from the incomplete decomposition of the starting material $AuCl_3$. At 150 °C, $AuCl_3$ decomposes to AuCl which at higher temperatures dissociates into the elements. These AuCl crystallites could also be reduced completely to Au metal by treatment of this sample with H_2 at 300 °C.

Molten media methods

In this variation on the two-step method, the opened nanotubes are filled using a pure liquid media, typically a molten metal oxide or halide. The molten material must have a surface tension less than *ca.* 100–200 mN m^{-1} in order to be able to wet and fill the nanotubes.[19] This filling method usually results in the formation of long, continuous crystals which occupy the entire internal diameter of the nanotube, as has been observed previously for an unidentified oxide phase of Pb[5,20] and also V_2O_5.[21] This filling is unlike the discrete crystals obtained from solution methods. This difference may result from the removal of solvation spheres which surround each ion and occupy part of the nanotube cavity.

Using the molten salt technique, carbon nanotubes have been filled with MoO_3. In a typical procedure, MoO_3 was crushed with a sample of pre-opened tubes and heated in a sealed silica ampoule to 800 °C for 3 h.[22] Approximately 50% of the nanotubes were observed to be filled with long single crystals of MoO_3 usually several thousand Å in length (not shown).

Molten $ZrCl_4$, $KCl/CuCl_2$, and UCl_4 and KCl/UCl_4[17] have also been used to fill nanotubes. The air-sensitive halides UCl_4 and $ZrCl_4$ were observed by TEM as $U_xO_yCl_z$ and ZrO_2, after oxidation. In the case of ZrO_2, HRTEM examination of the sample indicated that a large number of nanotubes had been destroyed during the reaction. The bulk of the sample was composed of nanoparticles and long, finger-shaped graphitic shards. A HRTEM image showing a surviving nanotube in which ZrO_2 is encapsulated is presented in Fig. 3. Similar destruction of carbon nanotubes has been observed to occur when the molten media method is used with other metal halides which are strong Lewis acids (*e.g.* $TiCl_4$, $GaCl_3$).

Reactions inside nanotubes

Attempts to fill empty tubes with molten metals were unsuccessful, presumably because the surface tension of the metals was too high to wet and fill the tubes.[19] Therefore, an indirect strategy was adopted whereby samples of a metal complex

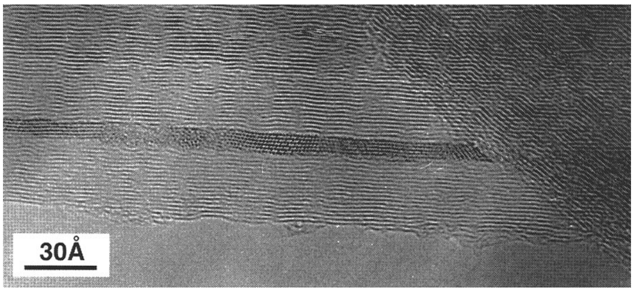

Fig. 3 A high-resolution TEM image of encapsulated polycrystalline ZrO_2. The observed lattices fringes (1,2) of 2.98 Å correspond to the distance between the (111) planes of the orthorhombic form of ZrO_2.

were first introduced into the nanotubes by one of the methods described above. The metal complex was then reduced to the elemental state by treatment with hydrogen gas at elevated temperatures. Fig. 4 shows a typical TEM image of a single crystal of nickel metal formed by reduction of an NiO crystal. The characterization of the reduced Ni metal sample was carried out by XRD and the direct determination of the distance between the lattice fringes of 2.05 ± 0.05 Å, which corresponds to the (111) spacing of Ni metal. This reaction may also be carried out starting directly from nickel nitrate filled nanotubes and treating them with H_2 as described above.

Using the same approach, encapsulated crystals of pure palladium and cobalt have been prepared.[3,18] Small crystallites of ruthenium metal located inside nanotubes are shown in Fig. 5. These crystallites are formed by treating ruthenium oxide samples with hydrogen. As can be seen in Fig. 5(a), the encapsulated Ru metal occurs as small, spherical crystals and as somewhat larger elongated crystals which grow along the axis of the nanotube cavities.

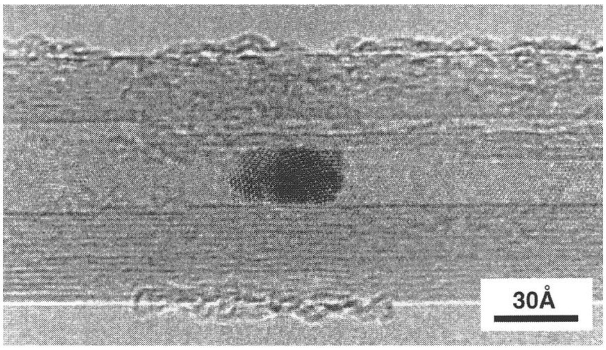

Fig. 4 A high-resolution electron micrograph of a nanotube filled with nickel metal, the faceting of the particles is typical of crystalline nickel metal. Sets of lattice fringes of 2.05 ± 0.05 Å corresponding to the (111) spacing in Ni metal can be clearly seen.

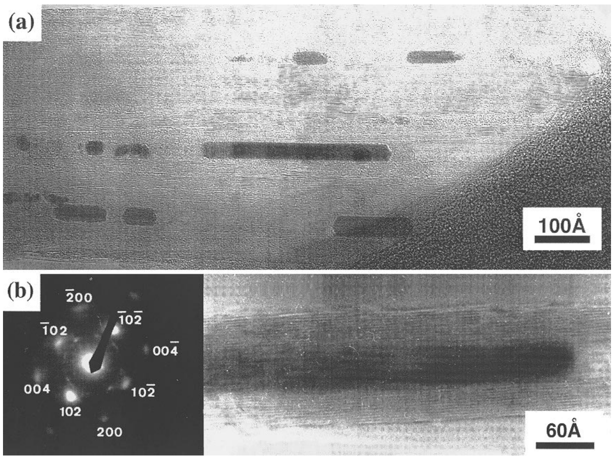

Fig. 5 (a) A high-resolution electron micrograph of nanotubes filled with both small spherical and elongated ruthenium metal particles. (b) HRTEM image and electron diffraction pattern (inset) obtained from encapsulated CdS. The indexing of the pattern is shown.

Another example of an *in situ* reaction is the formation of cadmium sulfide crystals from cadmium oxide by treatment with hydrogen sulfide at 400 °C. Electron diffraction obtained from encapsulated single crystals gave patterns which match well with CdS [Fig. 5(b)]. It is interesting to note that the obtained electron diffraction pattern corresponds to thermodynamically stable hexagonal CdS rather than the kinetic product, the cubic phase.

A related study was aimed at the preparation of high yields of nanotubes containing gold sulfide. First, pre-opened tubes were mixed with a concentrated solution of $AuCl_3$ in dry diethyl ether. After stirring for 24 h, the sample was treated with hydrogen sulfide in order to precipitate gold sulfide. Examination by TEM showed a high percentage of filled tubes (*ca.* 70%); however, there was also a large amount of material located outside the nanotubes. Fig. 6(a) shows a typical sample of nanotubes containing polycrystalline gold sulfide. The EDS analysis [Fig. 6(b)] shows a strong Au peak, with a clearly defined shoulder corresponding to sulfur. However, based on the information obtained from the EDS microanalysis and the fringe separations, a distinction between Au_2S and Au_2S_3 could not be made.

Conclusions

We have described several methods for the filling of nanotubes with metal oxides, pure metals and other materials. The identification of the encapsulated crystals was carried out by HRTEM and the direct imaging of lattice spacings, XRD and EDS. The nature of the filling is dependent on the method used to introduce the materials to the nanotube cavities, with both the one- and two-step methods giving discrete crystalline filling and molten media giving long, continuous crystals. We have also demonstrated that once encapsulated, materials may undergo reactions inside nanotubes. This finding suggests that filled nanotubes may find potential use in catalysis.

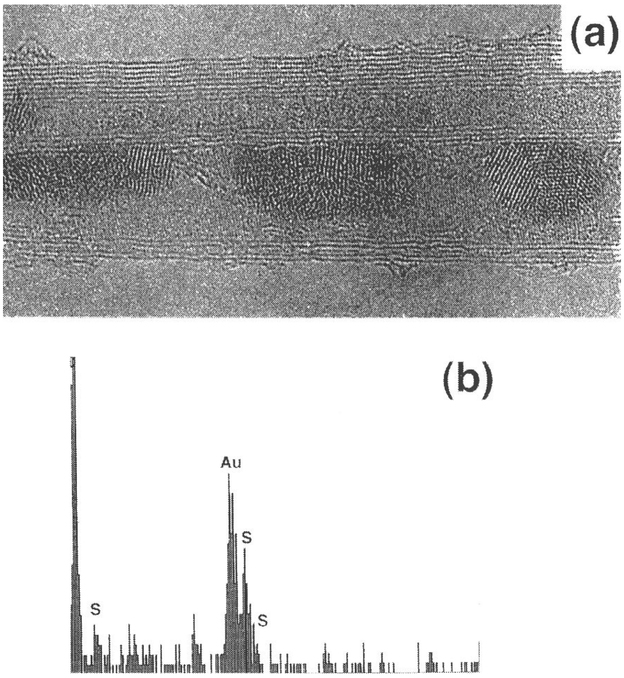

Fig. 6 (a) Nanotube filled with polycrystalline Au_xS_y particles (*ca.* 50 Å in length). (b) EDS microanalysis on the encapsulated material showing an Au peak and S shoulder indicating the formation of Au_xS_y.

We wish to thank Dr. J. L. Hutchinson and the Department of Materials for the use of JEOL 4000 EX and JEOL 2010 F microscopes and the Royal Society for a University Fellowship (S.C.T.).

References

1 T. W. Ebbesen and P. M. Ajayan, *Nature* (*London*), 1992, **358**, 220.
2 S. Iijima, *Nature* (*London*), 1991, **354**, 56.
3 S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, *Nature* (*London*), 1994, **372**, 159.
4 R. Seshadri, A. Govindaraj, H. N. Aiyer, R. Sen, G. N. Subbanna, A. R. Raju, and C. N. R. Rao, *Curr. Sci.*, 1994, **66**, 839.
5 P. M. Ajayan and S. Iijima, *Nature* (*London*), 1993, **361**, 333.
6 S. C. Tsang, J. J. Davis, M. L. H. Green, H. A. O. Hill, Y. C. Leung and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1995, 2579.
7 J. J. Davis, M. L. H. Green, A. O. Hill, Y. C. Leung, P. J. Sadler, J. Sloan and S. C. Tsang, *Eur. J. Biochem.*, 1996, in press.
8 S. C. Tsang, P. J. F. Harris and M. L. H. Green, *Nature* (*London*), 1993, **362**, 520.
9 P. M. Ajayan, T. W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki and H. Hiura, *Nature* (*London*), 1993, **362**, 522.
10 M. Liu and J. M. Cowley, *Carbon*, 1995, **33**, 225.
11 M. Liu and J. M. Cowley, *Carbon*, 1993, **33**, 749.
12 Y. Murakami, T. Shibata, K. Okuyama, T. Arai, H. Suematsu and Y. Yoshida, *J. Phys. Chem., Solids*, 1993, **54**, 1861.
13 S. Subramoney, R. S. Ruoff, D. C. Lorents, B. Chan, R. Malhotra, M. J. Dyer and K. Parvin, *Carbon*, 1994, **32**, 507.
14 Y. Yosida, *Appl. Phys. Lett.*, 1994, **22**, 64.
15 C. Guerret-Piécourt, Y. Le Bouar, A. Loiseau and H. Pascard, *Nature* (*London*), 1994, **372**, 761.
16 A. Chu, J. Cook, R. Heesom, J. L. Hutchison, M. L. H. Green and J. Sloan, *Chem. Mater.*, 1996, submitted.
17 J. Cook, J. Sloan, A. Chu and M. L. H. Green, in preparation.
18 R. M. Lago, S. C. Tsang, K. L. Lu, Y. K. Chen and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1995, 1355.
19 E. Dujardin, T. W. Ebbesen, H. Hiura and K. Tanigaki, *Science*, 1994, **265**, 1850.
20 P. M. Ajayan, T. W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki and H. Hiura, *Nature* (*London*), 1993, **362**, 522.
21 P. M. Ajayan, O. Stephan, P. Redlich and C. Colliex, *Nature* (*London*), 1995, **375**, 564.
22 Y. K. Chen, M. L. H. Green and S. C. Tsang, *Chem. Commun.*, 1996, 2489.

Paper 6/05652K; *Received* 13*th August*, 1996