The opening and filling of single walled carbon nanotubes (SWTs)

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Single walled nanotubes (SWTs) can be selectively opened and filled using wet chemistry techniques; treatment of the carbon nanomaterials with concentrated HCl apparently leads to the selective opening of the SWTs at their tips; foreign materials can then be deposited inside the resulting cavities in a similar fashion to multi-walled carbon nanotubes (MWTs); the filling of SWTs with small spherical crystals and, additionally, preferentially orientated and elongated single crystals of Ru metal is described; the selective opening of SWTs was inferred from these observations.

Multi-walled carbon nanotubes (MWTs) have attracted much interest since their discovery owing to their high mechanical strength and electrical properties.[1,2] They have already proved to be valuable in their application as tips for scanning probe microscopy and also as field emission devices.[3,4] The discovery and large scale synthesis of single-walled nanotubes (SWTs)[5,6] has given further impetus to this research as they similarly exhibit useful physical and electronic properties. SWTs can be generated by co-evaporating carbon and certain metals in arc-evaporation[5–9] or laser-vaporisation of metal-doped graphite[10,11] although they have also been produced by thinning of MWTs using CO_2.[12] SWTs display a higher degree of uniformity with respect to their physical dimensions compared to MWTs as they consist only of a single cylindrical graphitic layer and exhibit both a smaller range of diameters and far fewer defects than their multi-walled counterparts. Similarly, therefore, a greater degree of uniformity may be anticipated from their physical properties. Theoretical studies suggest that the introduction of foreign material into the inner cavities of MWTs or SWTs may enhance or modify the properties of the resulting composite materials.[13–15] Therefore, following similar work with MWTs,[16,17] we have employed wet chemistry techniques to open and fill SWTs. Here, however, a milder process has been used to selectively open SWTs since the oxidation methodology employed for opening MWTs[16] (*i.e.* refluxing concentrated HNO_3) was found to be too harsh for SWTs and resulted in their destruction.

The SWTs used in these experiments were produced in a modified arc-discharge chamber also employed to make MWTs.[14] Cobalt doped graphite rods were evaporated under a dynamic vacuum with helium (500 Torr) using an electric arc generated from a potential of 30 V and a dc current of 200 A. The external environment of the electrodes was confined by a 10 cm id steel cylinder 20 cm in length. The SWTs were found in the highest yield (*ca.* 30%) in the web-like material deposited on the walls of the cylinder. The diameters of the SWTs were found by high-resolution transmission electron microscopy (HRTEM) to be in the range 1–3 nm. For the filling experiments, samples of SWTs were suspended in concentrated HCl and stirred for 8 h. After centrifuging for 5 min, a light blue solution containing $CoCl_2$ was removed and the specimen was dried at 70 °C for 8 h and then washed with deionised water. A saturated solution of $RuCl_3$ (*ca.* 5 ml) was then added to the SWT-containing specimen and the mixture stirred for 5 h at 35 °C after which the black residue was dried at 60 °C overnight. The sample was then heated in a stream of H_2 at a rate of 5 °C min^{-1} to 45 °C and kept at this temperature for 3 h. After washing with distilled water and drying at 60 °C the residue was prepared for HTREM.

Electron micrographs revealed that a small proportion (*ca.* 5%) of the opened SWT contained foreign material. Fig. 1(*a*) shows a group of three SWTs, two of which apparently are filled with Ru crystals (arrowed). By slightly altering the defocus of the microscope, these crystals were observed to stay at the same focus with the SWTs and therefore we conclude that they are encapsulated inside the SWTs. As with studies carried out with MWTs,[17] individual crystallites were observed to fill the entire width of the hollow core of the SWTs as is seen in Fig. 1(*a*). Energy dispersive X-ray (EDX) microanalyses, utilising a 3 nm probe, performed on clusters of encapsulated crystallites similar to those in Fig. 1(*a*), confirmed their chemical identity as Ru metal [Fig. 1(*b*)], although some slight oxidation is apparent. Encapsulated and elongated crystallites were also frequently observed and these were again identified by EDX to be Ru metal. Fig. 2(*a*) shows an elongated Ru crystallite encapsulated near the elbow of a bent or damaged SWT. Fig. 2(*b*) shows an elongated Ru crystallite growing along the bore of one SWT at

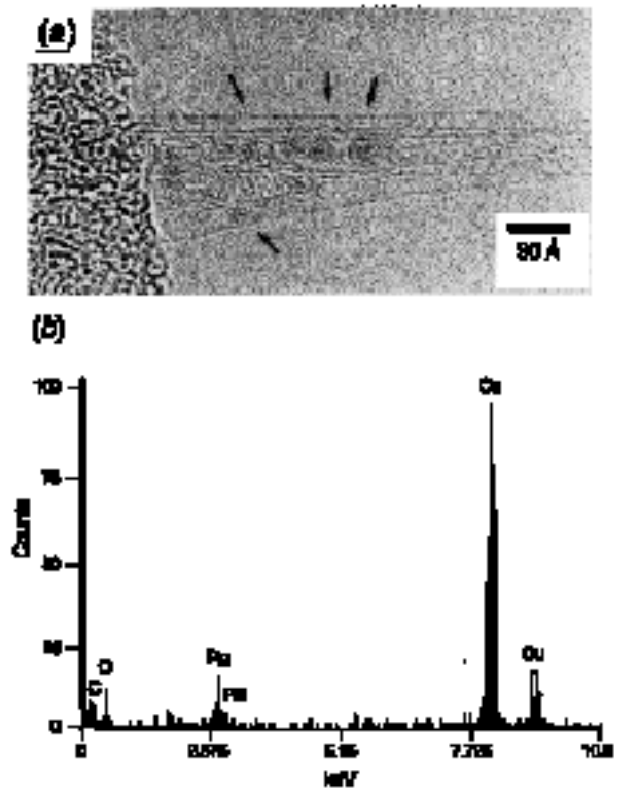

Fig. 1 (*a*) Individual Ru crystals encapsulated inside SWTs (arrowed). The diameter of the crystallites is apparently the same as that of the id of the SWT. (*b*) EDX microanalysis obtained from encapsulated Ru crystals similar to those observed in (*a*). O peak indicates that the crystallites are slightly oxidised. The Cu peak is from the copper TEM support grid.

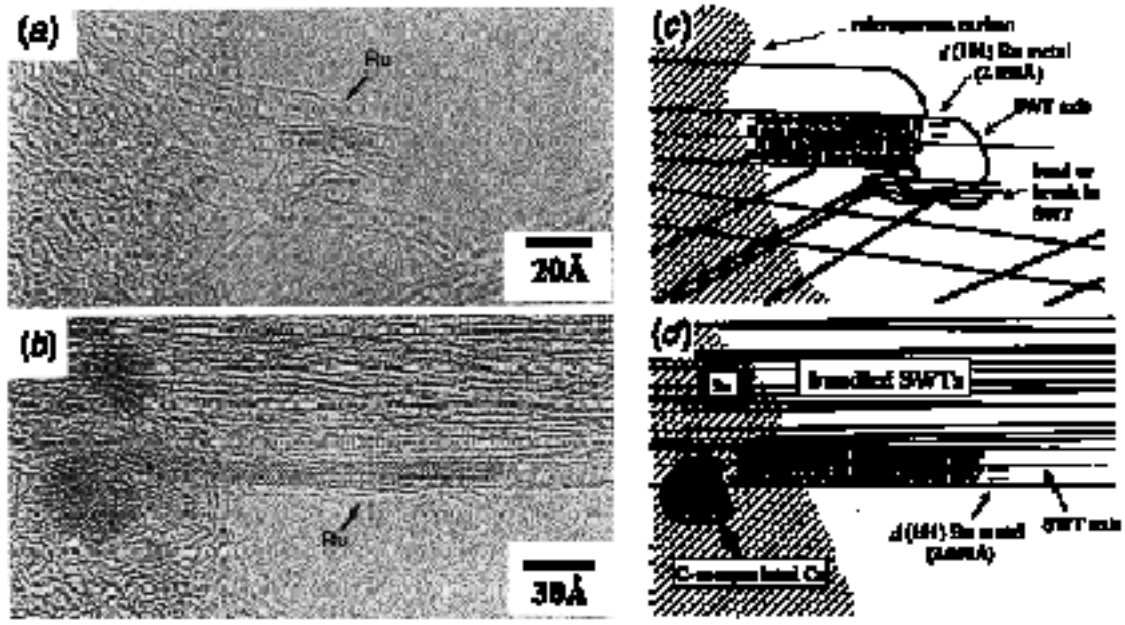

Fig. 2 (*a*) Elongated Ru crystallite encapsulated near the elbow of a bent or damaged SWT. The lattice fringes aligned parallel to the SWT axis corresponding to the *d*(101) lattice fringes of Ru metal. (*b*) Elongated Ru crystallite encapsulated inside a single SWT at the edge of a bundle of SWTs. As with the crystallite in Fig. 1(*a*), the *d*(101) Ru lattice fringes are orientated parallel to the SWT axis. (*c*) Schematic representation of (*a*). (*d*) Schematic representation of (*b*).

the edge of a bundle of SWTs (bundling of SWTs into 'ropes' is very common[10,11]). Both crystallites exhibit preferred orientations, with their *d*(101) lattice fringes[18] aligning parallel to the SWT axes. This phenomenon is represented schematically for Figs. 2(*a*) and (*b*) in Figs. 2(*c*) and (*d*), respectively. The phenomenon of preferred orientation inside SWTs is consistent with the observation of preferred crystallite orientation inside MWTs[19,20] and is most probably the result of the morphological influence of nanotube capillaries over crystallite growth during formation.[21] Other particles were also observed on the exterior of SWTs [Figs. 2(*b*) and (*d*)] and these were found by EDX to be either 'loose' Ru particles or carbon encapsulated Co particles which were presumably protected from acid attack by their carbon shells. It was not possible for us to conclusively image the opened tips of the SWTs by HRTEM because of their very low contrast compared to opened MWTs.[12] The selective opening of the SWTs was therefore inferred indirectly from the observation of their filling with Ru metal from solution which must have occurred in order for filling to occur. A further point is that we have not attempted to estimate the percentage of SWT opening in our experiments, partly for the above reason and also partly because the very high aspect ratio of SWTs would make this an extremely difficult proposition.

Experiments are currently under way in our laboratory to repeat this experiment with both ruthenium and other metals using a higher yield SWT method, similar to that recently reported by Journet *et al.*[22] We are also investigating methods for increasing the yield of the encapsulated product and are also trying to establish the mechanism by which opening occurs.

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Notes and References

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