A simple method for the containment and purification of filled open-ended single wall carbon nanotubes using C_{60} molecules†

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Soluble materials placed inside opened SWNTs can be contained using fullerenes to block the ends, thereby providing a way to remove the excess of external soluble material present in the initial product formed by low temperature filling of open-ended single wall carbon nanotubes; the C_{60}-blocked filled SWNTs can then be used in applications in which leakage is undesirable.

We have recently reported that opened single wall carbon nanotubes can be prepared from their closed counterparts on a multi-gram scale using steam at 900 °C.[1] These open-ended SWNTs can then be filled by, in effect, all materials stable at room temperature and soluble by simple mixing, as long as the surface tension of the filling liquid is less than about 170 mN m^{-1}.[2] Removal of the solvent, typically under reduced pressure, deposits the often crystalline solid involatile components inside and along the length of the SWNTs. The same solid material is similarly deposited outside the SWNTs since the open-ended and filled SWNTs, separated by filtration, cannot be washed without simultaneously washing away the soluble material from inside the filled, open-ended SWNTs.

There is considerable interest in filled SWNTs as the filling material can modify the properties of the SWNTs and have potential use in nano-electronic and nano-optoelectronic devices.[3] Also SWNTs filled with radioisotopes are envisaged as agents for *in vivo* imaging and tumour targeting.[4] SWNTs filled with Gd^{3+} have been studied for magnetic resonance imaging (MRI)[5] and I_2@SWNTs have been recently reported as an X-ray contrast agent.[6]

Most of the desired filled SWNT materials cannot be prepared at the high temperature conditions required for the melt filling method (typically >600 °C),[7] so the solution filling method is the most commonly used for low temperature filling. Therefore, for the envisaged applications it is necessary to be able to remove the excess of external soluble materials used in the filling experiment without removing the same material from inside the filled open-ended SWNTs. In all the examples detailed above, the encapsulated compounds should not be allowed to escape from within the filled SWNTs during their application. Furthermore, in the case of medical applications, an absence of material outside the SWNTs will reduce the side effects during targeting.

For these reasons a method for sealing up the ends of the open-ended SWNTs is required. Here we show that this can be achieved by simply using molecules of C_{60} to enter and block the ends of the previously open-ended filled SWNTs.

SWNTs made by chemical vapour deposition (CVD) were purified and opened to a high yield by treating them with steam[1] followed by heating in air.[8] The sample was then stirred in an aqueous solution of uranyl acetate; this was chosen as uranium is easy to detect using transmission electron microscopy (TEM). High resolution transmission electron microscopy (HRTEM) of the sample clearly showed the presence of a crystalline material inside and outside the SWNTs. Following the procedure described by Iijima *et al.* for filling C_{60} into the SWNTs (C_{60}@SWNTs),[9] the fullerene C_{60} in ethanol was added to the uranyl acetate filled SWNTs (uranyl acetate@SWNTs). The mixture was then stirred in aqueous hydrochloric acid, in which uranyl acetate is very soluble. After filtering and drying, the sample was examined by HRTEM and the continuing presence of uranyl acetate inside the SWNTs was confirmed whilst the uranium material outside the SWNTs had been removed. A more detailed HRTEM study of several individual SWNTs showed the presence of both C_{60} molecules and uranyl acetate crystals (Fig. 1).‡ The encapsulated uranium compound is presented in the form of short crystals along the SWNTs, characteristic of the solution filling method. Open ends of the SWNTs were also observed in the same sample. The C_{60} molecules are packed up to the very entrance, as shown in Fig. 1. HRTEM observation showed that C_{60} molecules were arranged in varied conformations depending on the tube diameter. Coalescence of C_{60} could also be observed during the HRTEM studies, which is a well-known phenomenon.

A blank experiment with uranyl acetate was made by repeating all the experimental procedures but without addition of C_{60}. After the final washing step with hydrochloric acid, no uranyl acetate could be detected either inside or outside the SWNTs and only empty SWNTs were observed by HRTEM. The fact that tubes filled with uranyl acetate after the HCl wash can be seen only when C_{60} is also present, confirms the ability of C_{60} to seal materials inside the SWNTs.

In order to check that the ability of C_{60} to plug the ends of open nanotubes was not unique to the uranium system we also studied the well-defined KI@SWNT system.[10] Purified arc-discharged SWNTs[1,11] were filled with molten KI at *ca.* 800 °C, giving KI@SWNTs with closed ends.[12] The SWNT

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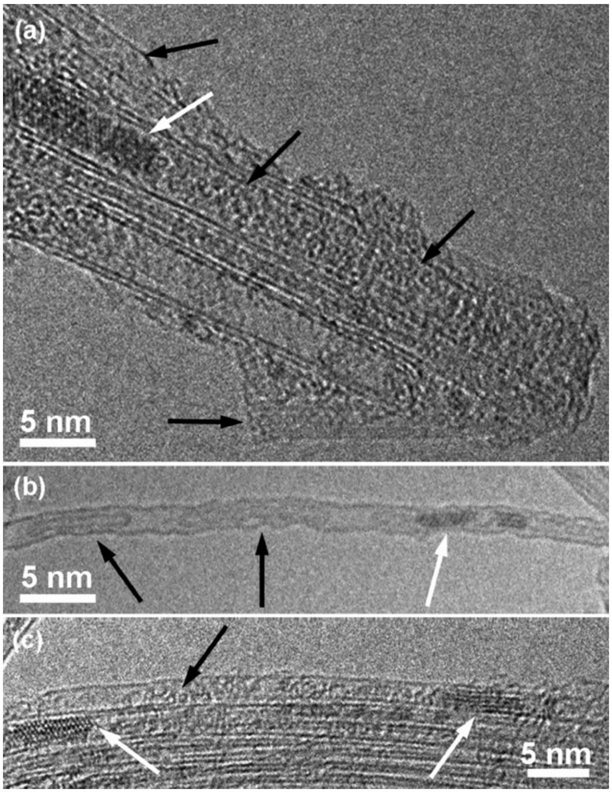

Fig. 1 HRTEM images of C_{60}-corked uranyl acetate filled SWNTs after being washed with HCl. As guides to the eye, white arrows point to the uranium compound, and black arrows point to some of the encapsulated C_{60} molecules.

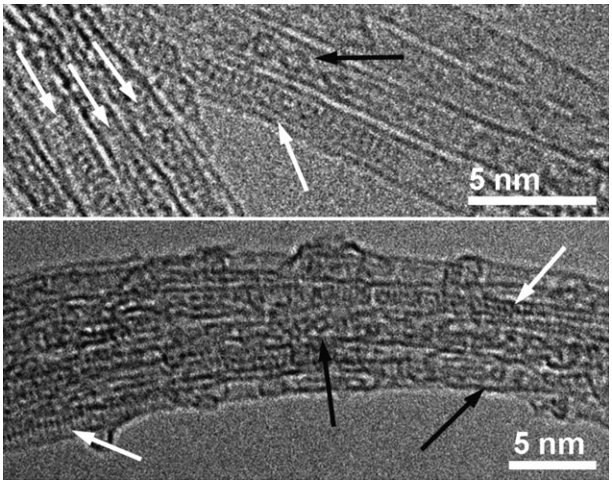

Fig. 2 HRTEM images of KI@SWNTs with C_{60} present after having been washed with water. As guides to the eye, the white arrows point to KI crystals, and black arrows point to some of the C_{60} molecules.

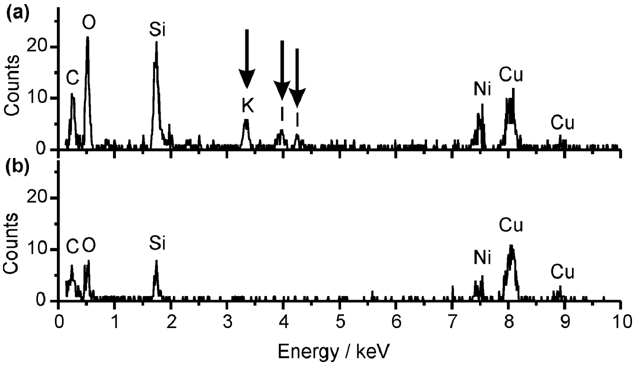

Fig. 3 EDX spectra of (a) KI@SWNTs containing C_{60} molecules, after being washed with water and (b) from a blank experiment of a sample of KI@SWNTs not treated with C_{60} after washing with water. The EDX spectra show the presence of Cu (TEM grid), Ni (catalyst for the synthesis of SWNTs) and Si and O (from the silica ampoule used in the filling experiment).

tips were then removed by heating the sample in dry air at 420 °C. A small portion of the oxidised sample was stirred in water and then analysed by HRTEM. Only empty tubes could be observed, confirming that the ends of the tubes had been successfully opened by the air treatment, allowing water to dissolve away the internal KI. The oxidised open-ended KI@SWNTs were treated with the vapour of C_{60} at 400 °C. The resulting C_{60}–KI@SWNT sample was then washed with hot water, filtered and dried. The HRTEM data showed high KI filling of the C_{60}–KI@SWNT sample and coexistence of both C_{60} and KI was observed in several individual SWNTs (Fig. 2). Energy dispersive X-ray (EDX) analysis of ten different areas confirmed the simultaneous presence of potassium and iodine (Fig. 3a). The fact that KI crystals were still present inside SWNTs after the washing in water, confirmed the ability of C_{60} to cork the ends of the SWNTs and prevent the solvent extraction of the encapsulated compound.

A blank experiment was made by repeating all the above steps without adding C_{60} to the sample of oxidised open KI@SWNTs. Only empty SWNTs were observed by HRTEM and EDX analysis (Fig. 3b).

In conclusion, we have described a simple and effective methodology to seal soluble materials inside open-ended SWNTs using C_{60} molecules, which have a strong affinity to enter the SWNTs,[13] as sealing agents.

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Notes and references

‡ Clearer images showing the simultaneous presence of both C_{60} and the uranium compound (or KI) inside SWNTs are difficult to obtain due to their different scattering nature.

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