CARBON NANOCAPSULES: BLOCKING MATERIALS INSIDE CARBON NANOTUBES

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Many compounds have been filled inside single-walled carbon nanotubes (SWNTs), including inorganic salts, organic molecules, fullerenes, metals and water. Unprecedented structures and properties have been observed for the encapsulated material [1], which can also alter the properties of the SWNTs [2]. Filled carbon nanotubes have potential use in nano-electronic and nano-optoelectronic devices. Also filled SWNTs are envisaged as promising agents for medical applications including *in vivo* imaging, tumour targeting and drug delivery.

The most commonly used methods for the encapsulation of materials in carbon nanotubes are solution, vapour and molten phase capillary filling. After the filling step, and regardless of the chosen method, a large amount of non-encapsulated material is present in the sample. A key step towards the characterisation and application of filled SWNTs is the complete removal of this unwanted external material whilst preserving the encapsulated payload (of the same nature). For instance, in the case of medical applications, the absence of species outside the SWNTs will reduce the side effects during targeting.

Here we present two complementary methodologies for the containment of soluble materials in the interior of SWNTs: closing the ends of SWNTs by thermal annealing [3] and using fullerenes as SWNT corks [4] (Figure 1).

SWNTs may be readily filled by direct heating to about 700-900 °C or higher in the presence of any material which is liquid and stable at that temperature and of which the liquid has a surface tension of less than about 170 mN/m [5]. On cooling the reaction mixture, the SWNTs are found to be filled with the chosen material and the ends of the filled SWNTs are closed [3]. We surmise that at high temperature the SWNTs spontaneously open to allow the molten materials to enter the SWNTs. On cooling, the openings in the CNT reclose and the internal material solidifies, often forming crystalline forms of filling material inside the CNTs. Since the resulting filled SWNTs are closed, the excess of the material external to the SWNTs may be dissolved away by choice of a suitable solvent. This high temperature filling method is limited mainly by the requirement that the chosen filling material is thermally stable as a melt, and for example, organic molecules can not be filled using this approach.

The alternative methods of filling SWNTs require that the closed as-made SWNTs first be opened at the ends. This can readily be accomplished by heating in steam at high temperature and then cooling in steam to room temperature [6, 7]. The resulting end-opened SWNTs may then be filled by solutions of the chosen material (ionic or covalent). Since the ends of the SWNTs remain opened, removal of the non-encapsulated material, external to the SWNTs would also result in the release of the encapsulated cargos. We have recently shown that fullerenes can be used as corks to block compounds inside open-ended SWNTs. The filled and blocked SWNTs can then be readily purified by stirring the sample in a suitable solvent. The reversibility of these “corks” is currently being studied. Potassium iodide and uranyl acetate have been used as model filling compounds since the highly scattering heavy elements, iodine and uranium are clearly visible by electron microscopy techniques. Recent results on the imaging of organic compounds encapsulated into SWNTs (erythrosine B and acetylsalicylic acid) will also be presented.

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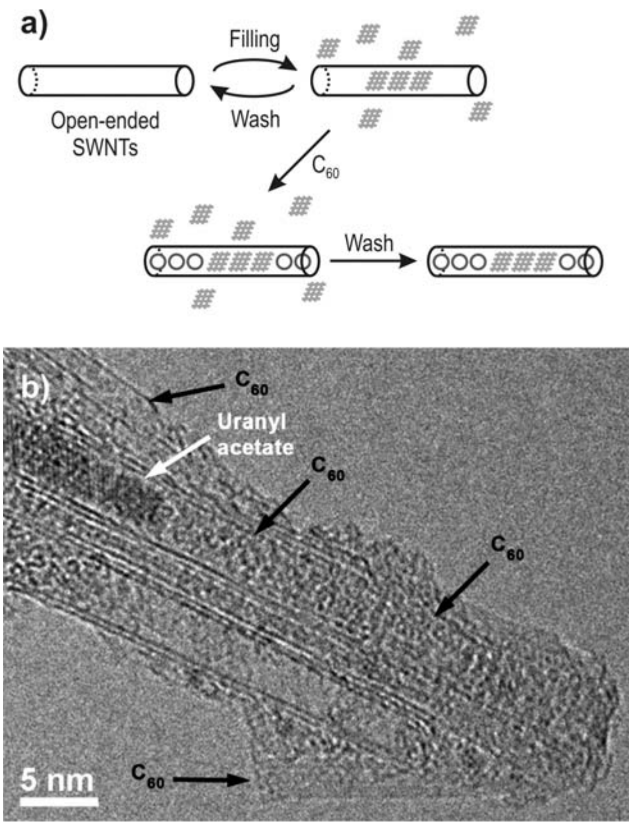
References:

[1] R.R. Meyer, J. Sloan, A.I. Kirkland, R.E. Dunin-Borkowski, M.C. Novotny, S.R. Bailey, J.L. Hutchison and M.L.H. Green, Science, 289 (2000) 1324.
[2] T. Takenobu, T. Takano, M. Shiraishi, Y. Murakami, M. Ata, H. Kataura, Y. Achiba, Y. Iwasa, Nat. Mater. **2** (2003) 683.
[3] L. Shao, G. Tobias, Y. Huh, M. L. H. Green, Carbon, **44** (2006) 2855.
[4] L. Shao, T.-W. Lin, G. Tobias, M. L. H. Green, Chem. Commun. (2008) 2164.
[5] E. Dujardin , T. W. Ebbesen, A. Krishnan, M. M. J. Treacy, Adv. Mater. **10** (1998) 1472.
[6] G. Tobias, L. Shao, C. G. Salzmann, Y. Huh, M. L. H. Green, J. Phys. Chem. B, **110** (2006) 22318.
[7] B. Ballesteros, G. Tobias, L. Shao, E. Pellicer, J. Nogués, E. Mendoza, M. L. H. Green, Small, **4** (2008) 1501.

Figure 1:



a) Schematic representation of the fullerene corking method and b) high resolution transmission electron microscopy of C_{60}-corked uranyl acetate filled SWNTs. *Reproduced from ref. [4] by permission of The Royal Society of Chemistry (RSC).*