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:


Figure 1:

a) Schematic representation of the fullerene corking method and b) high resolution transmission electron microscopy of C₆₀-corked uranyl acetate filled SWNTs. Reproduced from ref. [4] by permission of The Royal Society of Chemistry (RSC).