SYNTHESIS OF SWNT-BASED HYBRID NANOMATERIALS FROM PHOTOLOYIS-ENHANCED CHEMICAL PROCESSES

aMittal J., aMonthioux M.,a,b Allouche H.
a CEMES, UPR A-8011 CNRS, BP 4347, F-31055 Toulouse cedex 4, France
b LASEM, ENIS, Route de Soukra, 3038 Sfax, Tunisie

Introduction

Filling of inner cavities of single wall carbon nanotubes (SWNTs) may enhance or modify the properties of resulting hybrid materials. These filled SWNTs may also be useful as templates to produce low dimensionality conductive nanofibers as quantum wires. Evidences for successful filling of foreign materials into SWNTs were first reported in 1998 [1,2]. Since then, several preparation procedures have been proposed in literature, all of them involving thermal supply and/or peculiar atmosphere conditions (see for instance [3-8]). Here, we report very easy and simple ways of filling SWNTs with various materials such as chromium oxide (therefore forming CrOx@SWNTs [9]) and iron or molybdenum chloride, using chemical processes merely involving room temperature and open air atmosphere.

Further, filling SWNTs require to open them first. Most of the attempts to open SWNTs used inorganic acids (mainly HCl and/or HNO3) for either opening the nanotubes [2-3,5,8,10,11] or as a reactant for subsequent filling [9]. The present study also emphasizes UV-photolysis-based chemical processes as alternative methods to open (and possibly fill) SWNTs without using acidic treatments.

Experimental

A raw SWNT-containing collaret material prepared by electric arc method using a nickel-plus-yttrium-doped graphite anode was used as starting material [12]. Description of the starting material can be found elsewhere [13]. Briefly, it is made of SWNTs with regular diameters (i.e. with a diameter distribution centered on ~1.4 nm) associated with other carbon phases and catalyst particles. This material was treated with CrO3 and HCl (12M) in the molar ratio of 2:1 in open air at room temperature (~20°C) under natural light for one and two days. CrO3 has to be in large excess relative to the amount of SWNTs. The reaction products were washed with distilled water for removing unreacted mixtures of CrO3 and HCl.

Alternatively, the same raw SWNT material was subjected to UV treatment for 8 hours in presence of either chloroform, or a mixture of chloroform and MoCl5, or a mixture of chloroform and FeCl3. The UV radiation was not monochromatic but however had a wavelength spectrum centered on 253.7 as the main radiation, with an incident power in the range of ~100 W. Once the treatment time was over, unreacted products can be removed by washing with chloroform. The reaction products were recovered by evaporating the chloroform.

Structural investigation of the products was done using a Philips transmission electron microscope (HRTEM) operating at 120 kV, with a point resolution of 3 Å.

Results and Discussion

A representative example of the result from soaking the SWNTs after two-day treatment in CrO3 and HCl is given in Fig. 1. An isolated tube is shown instead of SWNT within a rope for sake of clarity, but similar features can be found in both situations. Between the nanotubes walls, a material is found to fill portions of the tube cavity. As a common observation [9], the filling material is separated from the tube walls on both sides by a gap consistent with van der Waals distances, indicating beyond any doubt that the foreign material is actually inside the tube rather than lying at the tube surface. Typically, the filling material is not found all along the tube, but as segments few nanometers long, often somewhat periodically distributed. However, the filling efficiency can be locally much higher, like in Fig. 1. Filling efficiency was estimated ~30% from a statistical TEM screening of many SWNTs, as the percentage of length of filled portions of SWNTs over the total length of SWNTs (i.e. filled or not) investigated. A specific EELS study using a 5 Å probe and a line scan mode demonstrated that the filling material is CrOx, possibly CrO3 [9]. Actually, the low difference in contrast between the filling material (containing Cr, whose Z = 24, but also O, whose Z = 8)
and the tube walls (containing C only, whose $Z = 6$), is consistent with a stoichiometry of the filling material such that O/Cr atomic ratio should be much higher than 1.

A suggested mechanism is that $\text{CrO}_2\text{Cl}_2$ was quickly formed in the solution due to the reaction of 12M HCl with $\text{CrO}_3$:

$$\text{CrO}_3 + 2 \text{HCl} \rightarrow \text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O} \quad (1)$$

Based on previous works performed on intercalated graphite [14], $\text{CrO}_2\text{Cl}_2$ is believed to intercalate between SWNTs within ropes. Occurrence of Cr, O and Cl atoms was actually found while analyzing SWNT ropes by X-photon energy dispersive analysis [9].

With the increase in time, $\text{CrO}_2\text{Cl}_2$ then started to slowly decompose, mainly under the effect of natural UV radiation, providing gaseous Cl$_2$, allowing the following reaction to attack the carbon from SWNTs walls:

$$2 \text{CrO}_2\text{Cl}_2 + \text{Cl}_2 + 2 \text{C} \rightarrow 2 \text{CrCl}_3 + 2 \text{CO}_2$$

$\text{SWNTs}$

(2)

The oxidation of SWNTs induced the local removal of carbon atoms from the SWNT walls, possibly promoted by pre-existing topological defects originating from the mechanisms of SWNT formation, as discussed elsewhere [15]. According to calculations [16], easily formed topological defects through C$_2$ dimer ingestion on side walls are twined pentagon-heptagon pairs (Fig. 4a). Since topological defects involving 5- and/or 7-type rings are energetically less stable than regular 6-type rings, they are likely to act as preferential sites for oxidation reactions. This created side openings in the tubes and subsequently allowed the highly concentrated chromium oxide solution to enter the SWNTs:

$$\text{CrO}_3 + \text{SWNTs} \rightarrow \text{CrO}_3@\text{SWNTs} \quad (3)$$

However, since direct stoichiometry quantification is not achieved yet, $\text{CrO}_3@\text{SWNTs}$ is preferred so far. The somewhat periodical distribution of the filling into the tubule cavity could then be related to a periodical occurrence of the pre-existing defects (or possibly surface impurities) on the SWNT walls.

On the other hand, using acids for opening and filling the tubes in solution method may be detrimental for SWNT structure [17]. Alternate methods were therefore considered. In one of these methods, SWNTs were treated with CHCl$_3$ added with FeCl$_3$ or MoCl$_5$ in presence of UV for 8 hours. Again, partial filling of SWNTs was achieved. Examples are imaged in TEM micrographs of Figs. 2 and 3. Chemical identification of both foreign materials was not completed by the time this paper was written, but again, considering the contrast of the filling material relative to that of the SWNT carbon walls, chances are high that they both contain Fe ($Z = 26$).
and Mo (Z = 42) respectively, both associated with lighter atoms (presumably Cl, whose Z = 17) so that the Cl/Fe and Cl/Mo atomic ratios are > 1.

**Figure 2.** HRTEM micrograph showing filled single wall nanotubes (diameter ranges from 1.2 to 2.3nm) after treatment with chloroform and FeCl₃ in presence of UV.

**Figure 3.** HRTEM micrograph showing filled single wall nanotube (diameter≈1.5nm) after treatment with chloroform and MoCl₅ in presence of UV.

The first step of the suggested mechanism (Fig. 4) for this second batch of experiments is the formation of dichlorocarbene (:CCl₂) originating from CHCl₃ dissociation due to UV irradiation:
Dichlorocarbene moieties might first graft onto neighboring carbon atom pairs from SWNT walls (preferably those involved into topological defects) so that they form bridges over C-C bonds (Fig. 4b) following a mechanism similar to that of the addition of diazo-compounds (e.g. diazomethane) to fullerene molecules [18]. According to the latter mechanism, the presence of such CCl₂ bridge/C-C bond combinations might result in opening C-C bond, specifically those involved in 5-6 ring junctions. It is therefore likely that twined pentagon-heptagon pairs offer multiple weak sites for preferable chlorocarbene addition and subsequent C-C bond opening (Fig. 4c). With the increase in treatment time and under UV irradiation, bridging CCl₂ might also be removed while C-C bonds involved remain open, finally resulting in wide entry ports (Fig. 4d) for subsequent filling of SWNTs by the solvated material present (FeCl₃ and MoCl₅ in the present work).

Further research work regarding the increase in the filling yield, reaction mechanisms, etc. are currently in progress.

Conclusions

The study provides the clues for the synthesis of new SWNT-based, hybrid nanomaterials. One of them is the first example ever of a filling based on metal oxide (CrO₃@SWNT). The latter result was achieved using a very simple experimental procedure, i.e. involving ambient conditions (room temperature and air atmosphere).

An alternative route for opening and eventually filling SWNTs using a liquid phase process not involving any acidic treatment has been discovered. The opening mechanisms include the formation of chlorocarbene due to the action of UV radiation on CHCl₃, and emphasizes the occurrence of pre-existing topological defects on side walls of SWNTs.

Acknowledgements

Authors thank Department of Chemistry of CNRS (France) for providing the Associate Researcher position to JM.

References

[12] Kindly obtained from P. Bernier, GDPC, University of Montpellier II, France