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# Fullerene derivatives encapsulated in carbon nanotubes

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We report on the preparation and subsequent Raman analysis of carbon nanotube peapods, using the fullerene  $C_{60}$  and its heterofullerene derivative  $(C_{59}N)_2$  as filling materials. The filling with  $(C_{59}N)_2$  was done from liquid solution at room temperature and from the gas phase at elevated temperatures. The success of the encapsulation procedure is confirmed through the identification of fingerprint Raman modes and the conversion to double wall nanotubes through heating to 1250 °C. The 2D mode of double wall nanotubes made from  $(C_{59}N)_2$  peapods is observed to be downshifted compared to the same mode in double wall nanotubes made from  $C_{60}$  peapods. We interpret this downshift as an evidence for the integration of the nitrogen into the lattice of the inner tube.

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# 1 Introduction

Since the pioneering works of Luzzi [1] the filling of single wall carbon nanotubes (SWCNTs) with various molecules established itself as one of the most promising sample preparation methods in nanocarbon research. This is due to the structure of the SWCNTs whose clean, homogeneous and chemically inert inner surface provides a favourable environment for the study of many physical and chemical properties of the in-filled molecular species.

Of special interest are spin carrying molecules, since their encapsulation in SWCNTs should give rise to 1-dimensional spin chains. Such low dimensional systems often display extraordinary physical behaviour. One possibility of a spin carrying molecule is  $C_{59}N$ , a radical that stabilizes through dimension to  $(C_{59}N)_2$  [2], or by aquiring a side group of various form.

Filling of SWCNTs with a  $C_{59}N$ , which had a sidegroup attached to one of the carbon atoms ( $C_{59}N$ -der) was already demonstrated in [3, 4]. In this works a new filling method was used, employing  $C_{59}N$ -der in solution and thus avoiding the high temperatures of the usual gas phase filling methods.

Here we report on an extension of this work by using unmodified  $(C_{59}N)_2$ , and two different solvents. For comparison,  $C_{60}$ -peapods were prepared and analyzed along the same routines. In addition, first results on filling SWCNT with  $(C_{59}N)_2$  from the gas phase are presented. We show that  $C_{59}N$ -peapods can

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be converted into double wall carbon nanotubes (DWCNT) by heating to 1250 °C. The chirality of the inner tubes is deduced from their Raman spectra. Finally an analysis of the 2D modes of the DWCNTs leads us to the conclusion that the nitrogen is incorporated into the inner tube walls.

# 2 Experimental

The SWCNT used were synthesized by the DIPS (direct injection pyrolytic synthesis) method, at the National Institute for Advanced Industrial Science and Technology (AIST), Tsukuba, Japan [5]. DIPS-nanotubes have a very low number of structural defects and are also of very high purity of up to 97.5%. The diameter distribution is rather broad, around a mean diameter of 1.6 nm to 1.7 nm.  $(C_{59}N)_2$  was prepared and isolated by the usual procedures [6].

Filling the nanotubes from the liquid phase was done by adding opened SWCNTs to a 1 mg/ml fullerene-toluene or fullerene-*n*-hexane solution and sonicating for 10 hours. The resulting material was filtered and dried. To remove non-encapsulated fullerenes the sample was heated at 650 °C in dynamic vacuum for 90 minutes. To induce the transformation to DWCNTs the peapods were heated at 1250 °C for one hour.

Filling from the gas phase was done by placing a mixture of nanotubes and fullerenes in a quartz tube and subsequently evacuating and sealing it. The sealed tube was then heated at 650 °C for 1 hour. Not encapsulated fullerenes were removed as described above. For  $(C_{59}N)_2$  the gas phase filling method did not work properly due to  $(C_{59}N)_2$  instability. Instead a new method as described below was developed. Raman spectra were recorded with a Dilor *xy* triplemonochromator spectrometer.

### **3** Results

The Raman response from encapsulated fullerenes is known to be much weaker than from the bulk material. So the analysis focusses naturally on the pentagonal pinch mode (PPM), the strongest mode in both  $C_{60}$  and  $C_{59}N$ . A comparison of the line position for encapsulated and non-encapsulated species is presented in Fig. 1.

In the bulk material we observe the PPM for  $(C_{59}N)_2$  at 1463 cm<sup>-1</sup> and for  $C_{60}$  at 1469 cm<sup>-1</sup>. The liquid solution filled and the gas phase filled peapods give the same positions: 1459 cm<sup>-1</sup> for  $(C_{59}N)_2$ , 1466 cm<sup>-1</sup> for  $C_{60}$ . Since  $C_{59}N$  enters into the gas phase as a monomer [7] this indicates a redimerisation to  $(C_{59}N)_2$ 



**Fig. 1** (online colour at: www.pss-b.com) (A) Pentagonal pinch mode (PPM) of non-encapsulated fullerenes. (B) The same spectral range for the encapsulated species, filled from liquid solution. (1) Filled with a 1:1 mixture of  $C_{60}$  and  $(C_{59}N)_2$ . (2) Filled with  $(C_{59}N)_2$ . (3) Filled with  $C_{60}$ . Note the slight downshift of the PPMs compared to (A) (see text). (C) Filled from the gas phase. (1) With  $(C_{59}N)_2$ . (2) With  $C_{60}$ . All spectra recorded with 488 nm excitation and at 85 K.

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inside the tube. With a value of 4.5 cm<sup>-1</sup> the encapsulation induced downshift is slightly larger in case of  $(C_{59}N)_2$ , as compared to 3 cm<sup>-1</sup> for  $C_{60}$ . The  $H_g(7)$  derived modes of  $(C_{59}N)_2$  span the range from 1420 cm<sup>-1</sup> to 1450 cm<sup>-1</sup> [8]. They give rise to a broader structure in the  $(C_{59}N)_2$  spectra compared to those of  $C_{60}$  since the lower symmetry of the  $(C_{59}N)_2$  molecule lifts the degeneracy. The spectral response from the  $H_g(7)$  modes is also different for the liquid filled and the gas filled samples. The  $H_g(7)$  derived modes appear to be stronger in the liquid filled sample. This could be the effect of an interaction with the also enclosed toluene molecules.

A final comment on Fig. 1c. The standard way of preparing a gas phase filled peapod sample does not work with  $C_{59}N$  since the unencapsulated molecule is not stable at 650 °C for the necessary time (1 hour). Reducing the temperature did not work either, since, as experiments (not shown) indicate, on lowering the temperature the filling time increases faster (lower gas pressure) than the decay of  $C_{59}N$  decreases. The other route is to increase the temperature and shorten the exposure time. The spectrum in Fig. 1c was taken from a so prepared sample. The evacuated and sealed quartz tube, filled with open SWCNTs and  $(C_{59}N)_2$ , was repeatedly heated in a gas flame. Typically after just a view seconds the  $(C_{59}N)_2$  evaporated and sublimated on some colder parts of the quartz, aside from the flame. A fraction entered the SWCNTs. This process was repeated for about 2 minutes.  $C_{59}N$  on the outside of the tubes was removed through heating at 650 °C in dynamic vacuum. Here it comes to bear that  $C_{59}N$  *inside* the tubes is stabilized by the tube walls and survives the procedure.

Figure 2 depicts Raman spectra of DWCNTs made from peapod samples as indicated. The lower intensities for  $(C_{59}N)_2$  derived inner tubes indicate a lower filling concentration for this species. This is not surprising since the azafullerene retains its dimeric form in solution. Due to their elongation, the dimers may well have a disadvantage on entering the tubes. Still the line position and overall structure of the radial breathing modes (RBM) of the inner tubes is almost the same for  $C_{60}$  and  $C_{59}N$  made DWCNTs. This indicates that both species entered SWCNTs of the same diameters. The only difference are the inner tubes of the largest diameter, with chirality (7,6). They are less prevalent in the  $(C_{59}N)_2$  grown DWCNTs.

The transformation of  $C_{59}N$  to an inner tube opens the question on what happens to the nitrogen. An incorporation into the lattice may lead to frequency shifts in the Raman spectra. The frequency of molecular vibrations is mass dependent, as can be seen e.g. through  ${}^{12}C \rightarrow {}^{13}C$  substitution. In a simplified approach, assuming a harmonic oscillator model and no change of the force constants via the incorporation of nitrogen, the frequency is proportional to the inverse of the square root of the mass. For the substitution  $C_{60} \rightarrow C_{59}N$  this gives a frequency shift of approx. 0.14%. Such a small shift is best observed on high energy modes. The Raman response of the 2D mode, the highest frequency mode of the strong



**Fig. 2** Transformation to double wall nanotubes (DWCNT). (1) DWCNT from  $C_{60}$ @SWCNT filled from a toluene solution. (2) DWCNT from  $(C_{59}N)_2$ @SWCNT filled from a toluene solution. (3) DWCNT from  $(C_{59}N)_2$ @SWCNT filled from a *n*-hexane solution. The inner tube modes originate from tubes with chiralities (*m*,*n*) as indicated.

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**Fig. 3** (online colour at: www.pss-b.com) 2D mode from double wall nanotubes at 514 nm laser excitation.

nanotube modes, is presented in Fig. 3. The signal is decomposed into the response from the inner and the outer tubes. The fit for the outer tube 2D mode was done on a SWCNT sample and the parameters adopted for the DWCNT fits.

The arrows in Fig. 3 mark the 2D peak originating from the inner tubes. For 514 nm laser excitation the observed downshift is 6 cm<sup>-1</sup>. Similar experiments were performed for 1064 nm excitation. In this case the downshift for the inner tube 2D mode was 3 cm<sup>-1</sup>. For comparison: Our simple model predicts a downshift of  $3.5 \text{ cm}^{-1}$ . We interpret the observed downshift as evidence for the integration of nitrogen into the inner tube walls. This result demonstrates that the system  $(C_{59}N)_2$  behaves different when transformed to DWCNT as compared to the system where a functionalized monomer is used for the growth of the inner tubes [3].

# 4 Conclusion

We have presented several different procedures to fill  $(C_{59}N)_2$  into SWCNTs. Filling from a liquid solution at room temperature is possible with either toluene or n-hexane as solvent. Filling from the gas phase needs a short time, high temperature method.  $(C_{59}N)_2$  can be converted to an inner tube. Our analysis of those inner tube RBMs strongly suggests that  $(C_{59}N)_2$  enters tubes of the same diameter range as  $C_{60}$  does. Finally our analysis of the 2D mode shift indicates the incorporation of nitrogen into the inner tube wall.

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