

Encapsulating C₅₉N azafullerene derivatives inside single-wall carbon nanotubes

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Abstract

Filling of single-wall carbon nanotubes with C₅₉N azafullerene derivatives is reported from toluene solvent at ambient temperature. The filling is characterized by high-resolution transmission electron microscopy and Raman spectroscopy. The filling efficiency is the same as for C₆₀ fullerenes and the tube-azafullerene interaction is similar to the tube-C₆₀ interaction. Vacuum annealing of the encapsulated azafullerene results in the growth of inner tubes, however no spectroscopic signature of nitrogen built in the inner walls is detected.

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1. Introduction

The hollow space inside single-wall carbon nanotubes (SWCNTs) have attracted considerable attention recently. The field was opened by the discovery of C₆₀ fullerenes encapsulated inside SWCNTs, the peapods [1]. Later it was found that chemical reactions can take place inside the tube such as charging induced polymerization [2] or fusion of the C₆₀ spheres to inner tubes [3,4]. The resulting inner tubes in the double-wall carbon nanotubes (DWCNTs) were shown to be exceptionally defect free [5] which apostrophizes the inside of the tube as “nanoclean-room chemical reactor”. We recently found that chemical reactions are not restricted to fullerenes but organic solvents such as benzene or toluene can also participate.¹ The breakthrough to further explore the in-the-tube

chemistry was the discovery of encapsulating fullerenes or fullerene derivatives at ambient temperatures [6–10]. Conventional peapod synthesis involves heating the sample above 400–500 °C [11,12], which most fullerene derivatives do not tolerate. C₅₉N, the on-ball nitrogen doped modification of fullerenes, has a rich chemistry due to its enhanced reactivity as compared to pristine fullerenes and can be synthesized in macroscopic amounts chemically [13,14]. The electronic state of C₅₉N and its derivatives is strongly modified compared to C₆₀ [15]. Encapsulating azafullerene peapods would be advantageous as they are expected to go preferably inside the SWCNTs similarly to all-carbon fullerenes, however their sizeable dipole moment adds a further degree of freedom for their applications such as e.g. ambipolar transistor [16]. In addition, the presence of the nitrogen enables to explore the in-the-tube chemistry with heteroatoms.

Here, we present the encapsulation of azafullerene derivatives inside SWCNTs. We use a low temperature synthesis method at ambient conditions. The encapsulation is proven by high-resolution transmission microscopy and Raman

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spectroscopy. The latter method shows that azafullerenes enter the tube with the same efficiency as C_{60} . Inner tubes grown from the azafullerene adduct are spectroscopically identical to all-carbon inner tubes.

2. Experimental

Commercial SWCNT (Nanocarblab, Moscow, Russia) was used in the current study. The SWCNT material is prepared by the arc-discharge method and is purified to 50 wt% by the manufacturer. The mean value, $d = 1.40$ nm, and the variance, $\sigma = 0.1$ nm, of the tube diameters were determined from multi-laser Raman measurements [17]. The starting azafullerene, $(C_{59}N)_2$, was prepared according to literature procedures [13]. The 4-hydroxy-3,5-dimethyl-phenyl-hydroazafullerene ($C_{59}N$ -der in the following) was prepared from 60 mg (41.66 μ mol) $(C_{59}N)_2$ and 135 mg (0.7 mmol, 10 eq.) p-Toluenesulfonic acid dissolved in 100 ml 1,2-dichlorobenzene. Forty-three milligram (351 μ mol, 5 eq.) 2,6-dimethylphenol was added to this solution. The reaction mixture was heated to 150 °C for 15 min while passing a constant stream of air through the solution. The formed product was isolated by flash chromatography using toluene as eluent. The product was precipitated from CS_2 /pentane, washed three times with pentane and dried in high vacuum and its molecular structure is shown in Fig. 1. The material was characterized by 1H and ^{13}C NMR and mass spectroscopy. Fullerene encapsulation was performed with the modification of the low temperature solvent method [8]: open SWCNTs were added to 1 mg/1 ml fullerene–toluene solutions and sonicated for 1 h in an ultrasonic bath (ELMA T460H, 35 kHz, 600 W power). The resulting material was filtered from the solvent, resuspended in excess toluene to remove non-encapsulated fullerenes and refiltered. Raman spectroscopy was performed on the bucky-papers. The material was then vacuum annealed at 1250 °C for 2 h for the growth of inner tubes from the encapsulated material following Refs. [3,4].

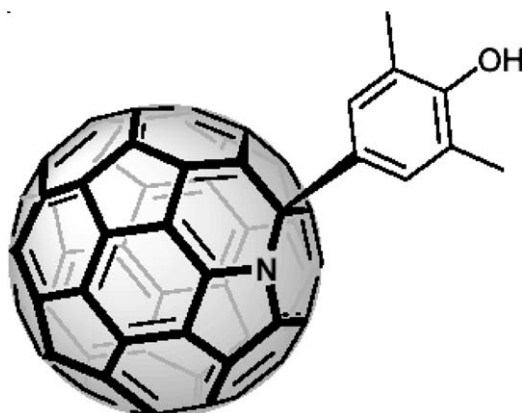


Fig. 1. Schematic structure of the 4-hydroxy-3,5-dimethyl-phenyl-hydroazafullerene.

High-resolution transmission electron microscopic (HR-TEM) studies were performed on a TECNAI F20 field emission microscope at 120 kV. The use of this voltage combined with low exposition times of 1 s allows to take good quality pictures without observable irradiation damage to the sample. HR-TEM samples were prepared from a suspension of the peapod material in N,N -dimethylformamide.

Raman spectroscopy was studied on a Dilor xy triple spectrometer in the 488–676 nm range with an Ar–Kr laser at room temperature. We used Raman spectroscopy to characterize the diameter distribution of the SWCNTs, to determine the concentration of encapsulated fullerenes, and to study the resulting DWCNT samples.

3. Results and discussion

In Fig. 2, we show a HR-TEM micrograph of the $C_{59}N$ -der encapsulated inside SWCNTs. HR-TEM shows an abundant filling of the tubes with the azafullerene, however it does not provide a quantitative measurement on the filling efficiency that is determined from Raman spectroscopy. A cross-section profile through the center of the encapsulated azafullerenes enables to determine their separation as the low and high values of the profile indicate bright and dark parts, respectively. Interestingly, we found 0.7–0.8 nm separation for some $C_{59}N$ -der pairs (indicated by arrows in Fig. 2) in contrast to the ~ 1 nm separation that is observed for encapsulated C_{60} peapods [1,18]. Although the data does not allow to determine the precise configuration of the $C_{59}N$ -der pairs, neither gives an accurate measure of their separation, it might be attributed to the presence of the strongly polar side-group of $C_{59}N$ -der.

In Fig. 3, we show the Raman spectra of the pristine and encapsulated $C_{59}N$ -der. The Raman spectra of the peapod sample (lower curve in Fig. 3) in the plotted frequency range consist of the SWCNT G modes around 1550 cm^{-1}

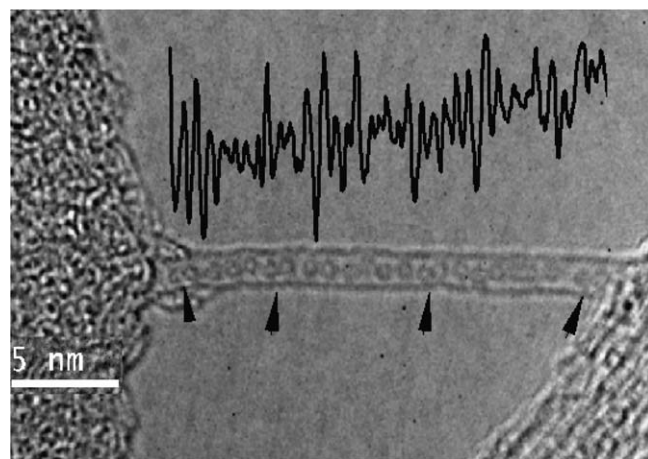


Fig. 2. HR-TEM micrograph of $C_{59}N$ -der encapsulated inside SWCNTs. The solid line shows a cross-section profile of the micrograph. Arrows indicate $C_{59}N$ -der pairs whose centers are only 0.7–0.8 nm apart.

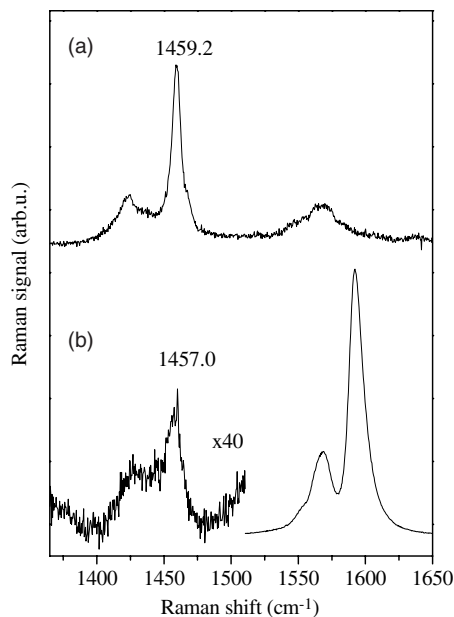


Fig. 3. Tangential mode of the Raman spectra of the $C_{59}N$ -der before (a) and after encapsulation (b) excited with a 488 nm laser. Labels mark the position of the strongest $C_{59}N$ -der mode in the two samples. The Raman G-mode of SWCNT dominates the peapod spectrum in the 1550–1650 cm^{-1} range.

and additional lines related to the Raman active modes of the encapsulated azafullerene derivative [2]. The major Raman modes of the pristine $C_{59}N$ -der are similar to those of the $(C_{59}N)_2$ dimer [19]. Here, we focus on the strongest mode that is observed at 1459.2 cm^{-1} . This mode is derived from the $C_{60} A_g(2)$ mode and is downshifted to 1457 cm^{-1} after the encapsulation procedure. The 2.2 cm^{-1} downshift proves the encapsulation of the molecule inside the SWCNT. When encapsulated inside SWCNTs, the corresponding $A_g(2)$ mode of C_{60} downshifts with 3 cm^{-1} , which is assigned to the softening of the $C_{60} A_g(2)$ vibrational mode due to the interaction between the ball and the SWCNT wall [2]. The slight difference between the downshift for the azafullerene and for the C_{60} peapods might be attributed to the different structure of the two molecules. The encapsulation also manifests in a line broadening: the main component of the 1457 cm^{-1} mode is broadened from 4.5 cm^{-1} FWHM in the pristine material to 10 cm^{-1} FWHM in the encapsulated one. This is similar to the values found for encapsulated C_{60} [2].

The integrated intensity of the observed $A_g(2)$ derived mode of the $C_{59}N$ is approximately 5 times larger than that of a C_{60} peapod prepared identically when normalized by the SWCNT G mode intensity. This, however, cannot be used to measure the encapsulation efficiency as Raman intensities depend on the strength of the Raman resonance enhancement and the Raman scattering matrix elements [20]. For C_{60} peapods the Raman signal was calibrated with independent and carbon number sensitive measurements: EELS studies gave the total number of C_{60} related and non- C_{60} related carbons [21] and the mass of encapsu-

lated C_{60} s was determined from NMR studies using ^{13}C enriched fullerenes [22]. In the current case, neither methods can be employed and we determined the filling efficiency for the azafullerene by encapsulating a mixture of the azafullerene and C_{60} .

In Fig. 4, we show the Raman spectra of the encapsulated $C_{59}N$ -der: C_{60} mixture with weight ratios of 1:9 in the starting solvent. The Raman spectrum of the encapsulated mixture was simulated with a weighted sum of the separately recorded spectra for encapsulated $C_{59}N$ -der and C_{60} . The best agreement between the simulated and the experimental spectra is for a $C_{59}N$ -der content of 0.12(2). This value is close to the expected value of 0.1 and it proves that the azafullerene enters the tubes with the same efficiency as C_{60} . The filling efficiency for C_{60} using the toluene stirring method was found to yield 48(1)% filling of the total available volume by comparing the Raman signal with the previous calibration [23]. This corresponds to $\sim 6\%$ fraction of the total sample mass as the 100% encapsulation corresponds to 13% mass fraction of the encapsulated fullerenes [22].

Encapsulating an azafullerene inside SWCNTs provides a unique opportunity to explore the in-the-tube chemistry with a heteroatom. Peapod samples with toluene encapsulated $C_{59}N$ -der and C_{60} were subject to 1250 $^{\circ}C$ dynamic vacuum treatment for 2 h. In Fig. 5, we show the Raman

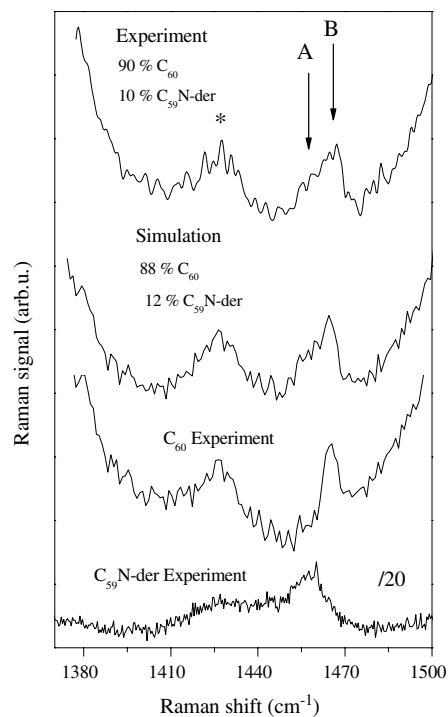


Fig. 4. Raman spectra of the encapsulated $C_{59}N$ -der: C_{60} mixture at the 488 nm laser excitation. The spectra for the $C_{59}N$ -der and C_{60} peapods is shown together with their weighted sum as explained in the text. A and B mark the components coming nominally from the superposing azafullerene and C_{60} phases, respectively. The asterisk marks a mode that is present in the pristine SWCNT material. Note the different scale for the $C_{59}N$ -der peapod material.

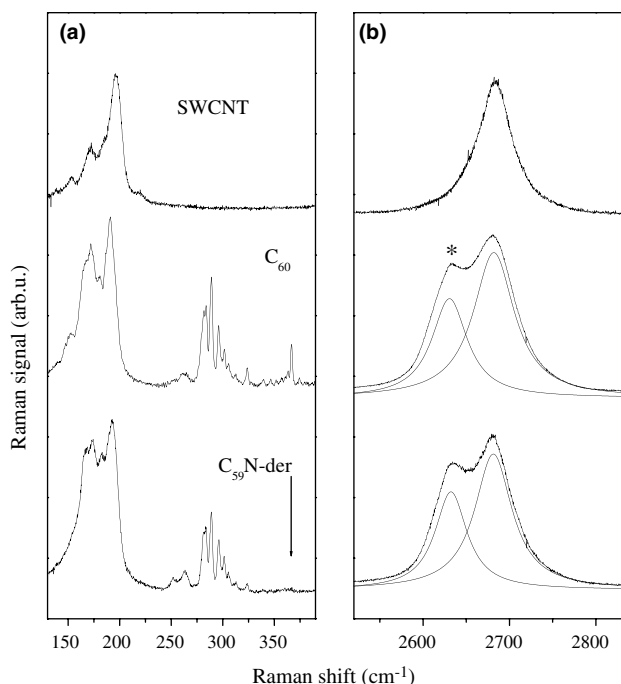


Fig. 5. Raman spectra of the DWCNTs made from C_{60} and $C_{59}N$ -der peapods with (a) 647 nm and (b) 515 nm laser excitation. The spectra of the starting SWCNT material is shown for comparison. Arrow indicates a small diameter RBM mode that is missing from the $C_{59}N$ -der based DWCNT sample. Solid curves show the deconvolution of the G' mode spectra into inner (marked by an asterisk) and outer tube mode components on (b).

response of the resulting DWCNT made from C_{60} and the $C_{59}N$ -der peapod samples. The radial breathing mode (RBM) range [24] is shown in Fig. 5a at 647 nm laser excitation and the Raman G' mode range in Fig. 5b with the 515 nm laser. For both materials, the narrow Raman lines in the $250\text{--}350\text{ cm}^{-1}$ spectral range correspond to the RBMs of inner tubes [5,25] and the lower frequency G' mode component (marked by an asterisk in Fig. 5b) to the inner tube G' mode [26]. The emergence of the inner tube RBMs and G' mode in the $C_{59}N$ -der peapod material is a further proof that the azafullerenes are indeed encapsulated inside SWCNTs. The G' mode is one of the most energetic vibrational modes of SWCNTs. Therefore, any effect related to the modification of the phonon energies would markedly manifest for this mode. We observe no change for the inner tube G' mode for the $C_{59}N$ -der based DWCNT as compared to the C_{60} peapod based DWCNTs. Thus, our result suggests that either nitrogen is not entering to the inner tube walls or it has no observable effect on the Raman spectrum.

The only difference observed for the $C_{59}N$ -der based DWCNT is the absence of some modes, corresponding to very small diameter inner tubes (shown by arrow in Fig. 5a). This can be understood by the somewhat larger effective size of the $C_{59}N$ -der compared to C_{60} and by its inability to enter in very small diameter SWCNTs. Since these tubes remain unfilled, they do not have an inner tube after the heat-treatment.

4. Conclusion

We presented the preparation of fullerene peapods containing a derivative of the azafullerene $C_{59}N$ with a low temperature synthesis method. The encapsulation efficiency of the azafullerene is the same as that of C_{60} fullerenes. Although no spectroscopic evidence for nitrogen on the inner tube walls was observed, our material is a starting point to explore the in-the-tube chemistry with heteroatoms. The material might find applications in nano-electronics as the presence of the sizeable electric dipole moment of the molecule allows to fine-tune the nanotube properties. Currently, we investigate the possibility of removing the sidegroup by thermal treatment to produce $C_{59}N$ monomer radicals embedded inside SWCNTs.

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References

- [1] Smith BW, Monthieux M, Luzzi DE. Encapsulated C_{60} in carbon nanotubes. *Nature* 1998;396:323–4.
- [2] Pichler T, Kuzmany H, Kataura H, Achiba Y. Metallic polymers of C_{60} inside single-walled carbon nanotubes. *Phys Rev Lett* 2001;87:267401–4.
- [3] Smith BW, Luzzi DE. Formation mechanism of fullerene peapods and coaxial tubes: a path to large scale synthesis. *Chem Phys Lett* 2000;321:169–74.
- [4] Bandow S, Takizawa M, Hirahara K, Yudasaka M, Iijima S. Raman scattering study of double-wall carbon nanotubes derived from the chains of fullerenes in single-wall carbon nanotubes. *Chem Phys Lett* 2001;337:48–54.
- [5] Pfeiffer R, Kuzmany H, Kramberger C, Schaman C, Pichler T, Kataura H, et al. Unusual high degree of unperturbed environment in the interior of single-wall carbon nanotubes. *Phys Rev Lett* 2003;90:225501–4.
- [6] Noé L, Monthieux M. Progrès sur la synthèse de $C_{60}@SWNTs$ (peapods) par voie liquide. In: Sixth National Colloquium of GDR n1752 CNRS on Carbon Nanotubes, Villeurbanne, France, 2003.
- [7] Yudasaka M, Ajima K, Suenaga K, Ichihashi T, Hashimoto A, Iijima S. Nano-extraction and nano-condensation for C_{60} incorporation into single-wall carbon nanotubes in liquid phases. *Chem Phys Lett* 2003;380:42–6.
- [8] Simon F, Kuzmany H, Rauf H, Pichler T, Bernardi J, Peterlik H, et al. Low temperature fullerene encapsulation in single wall carbon nanotubes: synthesis of $N@C_{60}@SWCNT$. *Chem Phys Lett* 2004;383:362–7.
- [9] Monthieux M, Noé L. Room temperature synthesis of $C_{60}@SWNT$ (peapods). In: XVIIIth international winterschool on electronic properties of novel materials. AIP Proceedings, 2004, Kirchberg, Austria, 2004.
- [10] Khloubystov AN, Britz DA, Wang JW, O'Neil SA, Poliakov M, Briggs GAD. Low temperature assembly of fullerene arrays in single-

- walled carbon nanotubes using supercritical fluids. *J Mater Chem* 2004;14:2852–7.
- [11] Smith BW, Monthieux M, Luzzi DE. Carbon nanotube encapsulated fullerenes: a unique class of hybrid materials. *Chem Phys Lett* 1999;315:31–6.
- [12] Kataura H, Maniwa Y, Kodama T, Kikuchi K, Hirahara K, Suenaga K, et al. High-yield fullerene encapsulation in single-wall carbon nanotubes. *Synth Met* 2001;121:1195–6.
- [13] Hummelen JC, Bellavia-Lund C, Wudl F. Heterofullerenes. *Topics in current chemistry*, vol. 199. Berlin: Springer; 1999. p. 93.
- [14] Hirsch A, Nuber B. Nitrogen heterofullerenes. *Acc Chem Res* 1999;32:795–804.
- [15] Pichler T, Knupfer M, Golden MS, Haffner S, Friedlein R, Fink J, et al. On-ball doping of fullerenes: The electronic structure of $C_{59}N$ dimers from experiment and theory. *Phys Rev Lett* 1997;78:4249–52.
- [16] Shimada T, Okazaki T, Taniguchi R, Sugai T, Shinohara H, Suenaga K, et al. Ambipolar field-effect transistor behavior of $Gd@C_{82}$ metallofullerene peapods. *Appl Phys Lett* 2002;81:4067–9.
- [17] Kuzmany H, Plank W, Hulman M, Kramberger C, Grüneis A, Pichler T, et al. Determination of SWCNT diameters from the Raman response of the radial breathing mode. *Eur Phys J B* 2001;22: 307–20.
- [18] Hirahara K, Bandow S, Suenaga K, Kato H, Okazaki T, Shinohara H, et al. Electron diffraction study of one-dimensional crystals of fullerenes. *Phys Rev B* 2001;64:115420–5.
- [19] Kuzmany H, Plank W, Winter J, Dubay O, Tagmatarchis N, Prassides K. Raman spectrum and stability of $(C_{59}N)_2$. *Phys Rev B* 1999;60:1005–12.
- [20] Kuzmany H. *Solid-state spectroscopy, an introduction*. Berlin: Springer; 1998.
- [21] Liu X, Pichler T, Knupfer M, Golden MS, Fink J, Kataura H, et al. Filling factors, structural, and electronic properties of C_{60} molecules in single-wall carbon nanotubes. *Phys Rev B* 2002;65: 045419–23.
- [22] Simon F, Kramberger C, Pfeiffer R, Kuzmany H, Zólyomi V, Kürti J, et al. Isotope engineering in carbon nanotube systems. *Phys Rev Lett* 2005;95:017401–4.
- [23] Kuzmany H, Pfeiffer R, Kramberger C, Pichler T, Liu X, Knupfer M, et al. Analysis of the concentration of C_{60} fullerenes in single wall carbon nanotubes. *Appl Phys A* 2003;76:449–55.
- [24] Dresselhaus MS, Dresselhaus G, Ecklund PC. *Science of fullerenes and carbon nanotubes*. San Diego: Academic Press; 1996.
- [25] Simon F, Kramberger C, Pfeiffer R, Holzweber M, Kuzmany H. The Raman response of double wall carbon nanotubes. In: Rotkin SV, Subramoney S, editors. *Applied physics of carbon nanotubes*. New York: Springer; 2005. p. 203–24.
- [26] Pfeiffer R, Kuzmany H, Simon F, Bokova SN, Obratsova E. Resonance Raman scattering from phonon overtones in double-wall carbon nanotubes. *Phys Rev B* 2005;71:155409-1–9-8.