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Encapsulating $C_{59}N$ azafullerenes inside single-wall carbon nanotubes

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Filling of single-wall carbon nanotubes with $C_{59}N$ azafullerene derivatives is reported from toluene solvent at ambient temperature. The filling is characterized by high resolution transmission electron microscopy and Raman spectroscopy. The tube–azafullerene interaction is similar to the tube–C_{60} interaction. The encapsulated $C_{59}N$ monomer radical is observed using electron spin resonance spectroscopy after vacuum annealing of the azafullerene derivatives.

1 Introduction

The hollow space inside single-wall carbon nanotubes (SWCNTs) has recently attracted considerable attention. The area was opened by the discovery of C_{60} fullerenes encapsulated inside SWCNTs, the peapods [1]. It was found that chemical reactions can take place inside the tube such as charge induced polymerization [2] or fusion of the C_{60} spheres to inner tubes [3, 4]. The breakthrough to further explore the in-the-tube chemistry was the development of fullerene encapsulation at ambient temperatures [5–9]. Conventional peapod synthesis involves heating the sample above 400–500 °C [10, 11], which most fullerene derivatives do not tolerate. $C_{59}N$, the on-ball nitrogen doped modification of fullerene, has a rich chemistry due to its enhanced reactivity as compared to pristine fullerenes and can be synthesized in macroscopic amounts [12, 13]. The electronic state of $C_{59}N$ and its derivatives is strongly modified compared to C_{60} [14]. 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 in e.g. ambipolar transistor [15]. $C_{59}N$ forms a non-magnetic dimer crystal, where the $(C_{59}N)_2$ units are non-magnetic singlets [12]. However, the magnetic $C_{59}N$ monomer radical can be stabilized when it is dilutely mixed in C_{60} [16]. It is expected that similarly, encapsulated $C_{59}N$ monomers might be magnetic if separated by C_{60}.

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 trans-

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mission microscopy and Raman spectroscopy. The latter method shows that the tube–azafullerene interaction is similar to the tube–C_{60} interaction. High temperature annealing removes the side-group giving rise to the ESR active $C_{59}N$ monomer radical.

2 Experimental

Commercial SWCNT (Nanocarblab, Moscow, Russia) grown with the arc-discharge method and purified to 50 wt% was used to synthesize the peapods. 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 standard procedures [12]. The 4-hydroxy-3,5-dimethyl-phenyl-hydroazafullerene ($C_{59}N$-der in the following) was prepared from 60 mg (41.66 µmol) $(C_{59}N)_2$ and 135 mg (0.7 mmol, 10 eq.) p-toluenesulfonic acid dissolved in 100 ml 1,2-dichlorobenzene. 43 mg (351 µmol, 5 eq.) 2,6-dimethylpenol was added to this solution. The reaction mixture was heated to 150 °C for 15 min while being in a constant air stream. The product formed was isolated by flash chromatography with toluene 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 [7]: 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, re-suspended in excess toluene to remove non-encapsulated fullerenes and re-filtered. Raman spectroscopy was performed on the bucky-papers. The material was then vacuum annealed at 1250 °C for 2 hours for the growth of inner tubes from the encapsulated material following Ref. [3, 4]. The peapods were annealed in dynamic vacuum at 600 °C for 15 min to remove the side-group. After this, the materials are air sensitive and were sealed under He in quartz tubes.

High resolution transmission electron microscopy (HR-TEM) was performed on a TECNAI F20 field emission microscope at 120 kV. Raman spectroscopy was done 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 and to determine the concentration of encapsulated fullerenes. ESR studies were performed with a microwave power of 0.1 mW and 0.02 mT magnetic field modulation in a Bruker Elexsys X-band spectrometer in the 10–600 K temperature range. This power and magnetic field modulation preserves the intrinsic ESR line-shapes.

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, however it does not provide a quantitative measurement of the

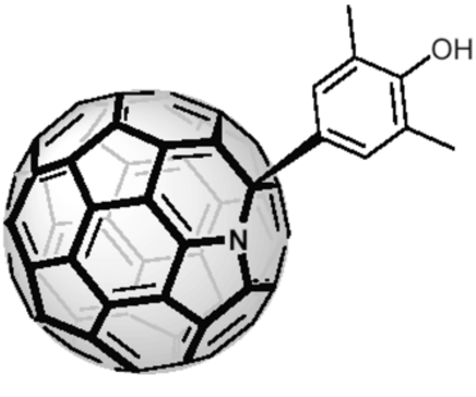

Fig. 1 Schematic structure of the 4-hydroxy-3,5-dimethyl-phenyl-hydroazafullerene.

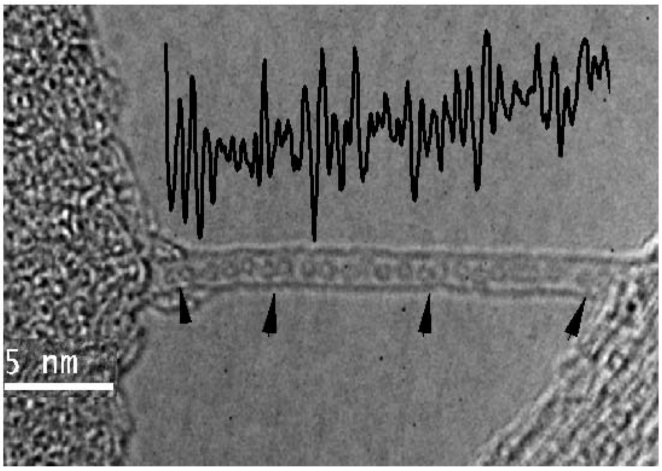

Fig. 2 HR-TEM micrograph of C_{59}N-der encapsulated inside SWCNTs. The solid line shows a cross-section profile of the micrograph. Arrows indicate C_{59}N-der pairs whose centers are only 0.7–0.8 nm apart.

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]. This 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} 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

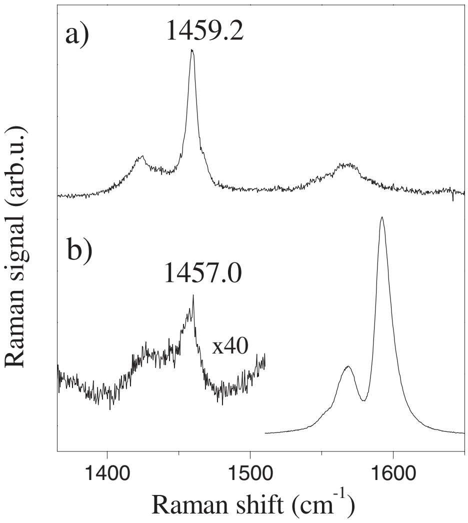

Fig. 3 Tangential mode of the Raman spectra of the C_{59}N-der before (a) and after encapsulation (b) excited with a 488 nm laser. Labels mark the position of the strongest C_{59}N-der mode in the two samples. The Raman G-mode of SWCNT dominates the peapod spectrum in the 1550–1650 cm^{-1} range.

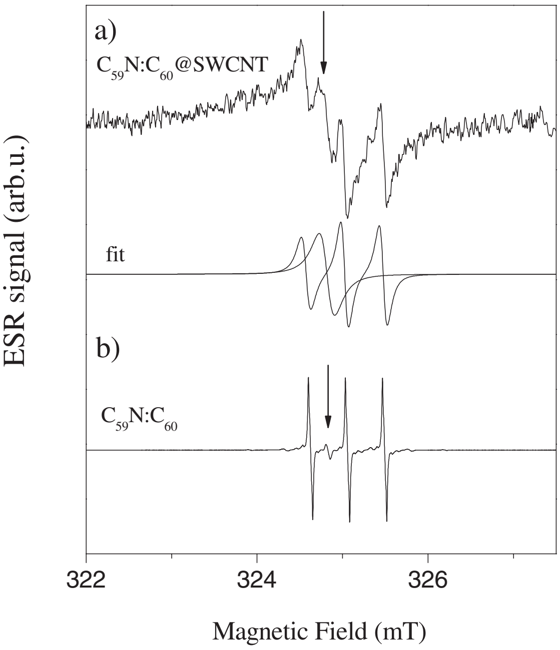

Fig. 4 ESR spectra of $C_{59}N:C_{60}$@SWCNT (a) and crystalline $C_{59}N:C_{60}$ (b) at 300 K. Arrows indicate the $C_{59}N-C_{60}$ heterodimer component. Solid curves show a deconvolution of the ESR signal into the triplet and the heterodimer components for the peapod material.

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].

In Fig. 4, we show the room temperature ESR spectra for the peapod sample after vacuum annealing and also for a crystalline $C_{59}N:C_{60}$ from Refs. [16, 20]. C_{60} was co-encapsulated together with the azafullerene derivative to separate the $C_{59}N$ monomers. The spectra consists of a ^{14}N ($I = 1$) hyperfine triplet and an additional line (arrows in Fig. 4) from $C_{59}N-C_{60}$ covalently bound heterodimers [20]. A triplet structure with somewhat asymmetric line-shapes and different line-widths is observed for the peapod sample. The hyperfine coupling constant of the triplet structure is identical for both samples within experimental precision and is thus identified as the ESR signal of rotating $C_{59}N$ monomer radicals.

The additional component observed for the peapod sample (arrow in Fig. 4a) is identified as a $C_{59}N-C_{60}$ heterodimer as it has an identical g-factor as in the crystalline material. For the peapod sample a broader line with $\Delta H_{pp} \sim 0.6$ mT is also observed. All ESR signals appear upon heat treatment only, however, the broader component is present in reference samples without encapsulated $C_{59}N$-der and is identified as a side-product. Annealing at 600 °C is the optimal heat treatment as smaller temperatures result in smaller triplet signal and higher temperatures only increase the broad impurity signal. The observation of encapsulated $C_{59}N$ monomer radical is the second example after the encapsulated N@C_{60} of an encapsulated magnetic fullerene [7, 9].

4 Summary

In summary, we presented the preparation of fullerene peapods with a derivative of the azafullerene $C_{59}N$ using a low temperature synthesis method. The encapsulation efficiency of the azafullerene is the same as that of C_{60} fullerenes. We observed the $C_{59}N$ monomer radicals embedded inside SWCNTs upon heat treating the azafullerene derivative peapods. The material is an important step toward the realization of confined linear spin-chains, which might find application in e.g. quantum information processing.

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