

Stability and electronic properties of magnetic peapods

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1 Introduction The peapod structure [1] is an intriguing modification of SWCNTs with a number of expected and proven fundamentally interesting and application oriented properties. The growth of peapods was studied with molecular dynamics simulations [2] and the existence of the structure was explained by the net energy gain per encapsulated fullerenes [3–6]. Peapods turned out to be a model system to study molecular interactions such as fullerene polymerization [7], guest-host interactions [8], and they are also the precursors to double-wall carbon nanotubes [9, 10] which enabled the growth of ¹³C isotope enriched inner tubes [11]. Concerning applications, peapods were found to show ambipolar field transistor effect [12] and modified field emission characteristics as compared to empty SWCNTs [13].

A particularly interesting class of peapods is that with encapsulated magnetic fullerenes such as metallofullerenes with magnetic rare-earth ions [12], the endohedral N@C₆₀ [14], and C₅₉N [15]. Peapods with magnetic fullerenes can be used to study the electronic properties of the tubes [15] and may be suitable for quantum information processing [16, 17] and they are thought to be good candidates for magnetic force microscopy cantilevers. However, both kinds of yet synthesized magnetic fullerene peapods have

drawbacks: the N@C₆₀ is available in a few hundred ppm concentrations only, thus a given nanotube contains a single magnetic fullerene on the average. More concentrated N@C₆₀:C₆₀ is available in micro- or nanoscopic amounts. In addition, the N@C₆₀ molecule is very sensitive to temperature and annealing to ~ 500 K irreversibly destroys it through the escape of the nitrogen [18]. The C₅₉N magnetic fullerene is available in macroscopic amounts [19], however adjacent molecules dimerize and the C₅₉N monomer radicals are air sensitive. Clearly, a magnetic fullerene, that is not air sensitive and is available in macroscopic amounts, is the best candidate for the encapsulation.

These aspects motivated the current work. Here, we report on the temperature stability of N@C₆₀ when it is encapsulated inside SWCNTs. In addition, we report on the synthesis of a novel magnetic fullerene peapod, a fullerene spin-labeled with a nitroxide radical.

2 Experimental We prepared peapods from commercial purified SWCNTs (Nanocarblab, Moscow, Russia, purity 50 wt%). The sample was heated in air at 450 °C for 10 minutes to open the tubes and to remove water and other absorbed materials from the inner space. The SWCNTs have an average tube diameter of 1.4 nm, which is

optimal for encapsulating fullerenes and fullerene derivatives. We also closed the openings on the tubes in control experiments, which was performed by annealing in dynamic vacuum at 1000 °C for 1 h following Ref. [20]. The endohedral fullerene was produced by the N implantation method [21] followed by high performance liquid chromatography to purify and concentrate the material to 400 ppm N@C₆₀:C₆₀. The nitroxide spin-labeled fullerene is the fullerene cycloadduct of 3,4-Bis(methylene)-2,2,5,5-tetramethylpyrrolidin-1-yloxy (FCTPNO in the following) that was synthesized following the previously published route [22]. Encapsulation was performed by suspending the SWCNT in toluene containing the dissolved magnetic fullerenes and sonicating for 2 hours followed by filtering with a 0.4 micron pore size filter and drying at room temperature to obtain samples in the form of bucky-papers. After degassing at room temperature, the bucky-paper samples were ground to enable penetration of the exciting microwaves and to avoid microwave losses. The samples were sealed in quartz tubes under He atmosphere. Experiments were carried out using a Bruker Elexsys E500 spectrometer with a TE011 microwave cavity equipped with gas-flow inserts for the high (300–620 K) temperature measurements. The ESR signal intensity, which is proportional to the number of spins observed, was determined by fitting Lorentzian curves to the data.

3 Results and discussion

3.1 Thermal stability of the N@C₆₀ peapods

The ESR spectra of the crystalline and peapod N@C₆₀:C₆₀ materials are shown for different temperatures in Fig. 1. A triplet signal, which is characteristic for the hyperfine interaction of the N spins with the ¹⁴N nucleus with nuclear spin $I = 1$ is observed for both kinds of samples. The three unpaired electrons on the 2p³ nitrogen atomic orbitals are in an S=3/2 state configuration. The zero-field splitting of the electron Zeeman levels is small due to the high symmetry of the fullerene cage and it can be observed in spin-echo ESR experiments only [23]. The isotropic nuclear hyperfine coupling, $A_{\text{iso}} = 0.565$ mT of N@C₆₀ is uniquely large due to the compression of the nitrogen orbitals, which unambiguously identifies the observation of this molecule [21].

Besides the triplet, the peapod spectra contains a broad background (not shown) due to the inevitable presence of ferromagnetic Ni:Y catalysts in the SWCNT samples. However, the peapod spectrum does not contain any impurity line around $g = 2$ as observed in the early studies [14], which attests the high SWCNT sample purity. The ESR signal intensity observed for the peapod sample was compared to that in the crystalline sample, which enables to determine the amount of N@C₆₀ in the peapods. We found that fullerene content in the peapod is ~ 2 –3 weight-percent, in agreement with the previous studies [14, 11].

The ESR signal intensity is a measure of the static spin-susceptibility. This follows the $1/T$ Curie temperature de-

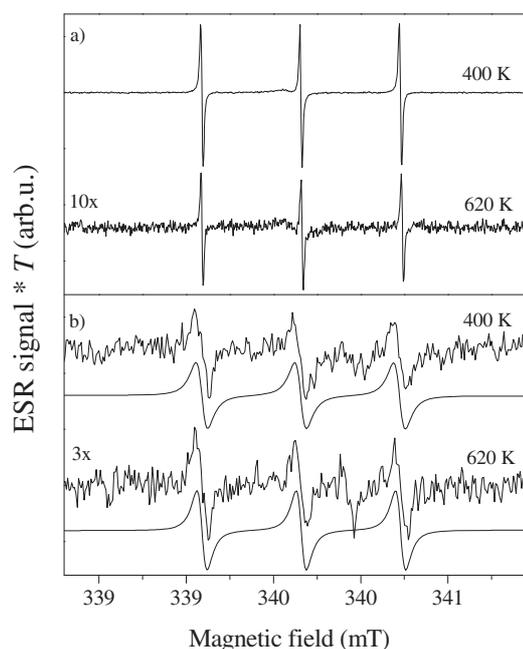


Figure 1 ESR spectra of the crystalline (a) and peapod (b) N@C₆₀:C₆₀ multiplied by the temperature to account for the Curie temperature dependence of the signal intensity. Note the magnified vertical scale for the high temperature data. Solid curves are fit to the data.

pendence for a dilute spin systems such as the one being investigated. Thus the number of N@C₆₀ spins observed, $N(T)$, is proportional to the product of the ESR signal intensity and the temperature. Since we are interested in the change of $N(T)$ as a function of temperature, normalizing it to a well defined temperature value allows a precise monitoring of the decay of N@C₆₀. In Fig. 2, we show the temperature dependence of the number of N@C₆₀ spins in both kinds of samples normalized to the value at 400 K. For comparison, we show the corresponding data from Ref. [18]. The annealing speed was 90 s/2 K, that is identical to the heating protocol used in Ref. [18]. At 580, 600, and 620 K, we performed longer data acquisition thus less temperature points were taken to maintain the annealing protocol. We observe a clear drop in the number of N@C₆₀ for the crystalline material when heated above ~ 550 K. However, we observe that the decay is less sharp and that it occurs at about 50 K higher temperature than that observed previously [18]. We have no clear explanation for this difference between ours and the previous studies.

The important result is that the number of N@C₆₀ does not decay in the peapod sample as fast as in the crystalline material. We observe relatively three times as much N@C₆₀ in the peapod material at 620 K than in the crystalline material. This effect is also apparent in Fig. 1, where the corresponding spectra are shown. Although the noise in the peapod data limits the conclusions, the decay of

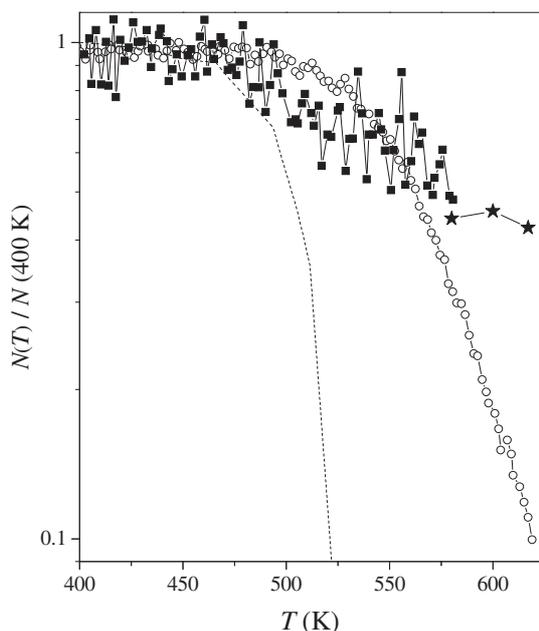


Figure 2 Temperature dependence of the number of $N@C_{60}$ spins, $N(T)$ normalized to the 400 K values, circles: crystalline, squares: peapod. The longer averaged data for the peapod material at 580, 600, and 620 K are shown with asterisks. Dashed curve shows data on the crystalline material from Ref. [18].

$N@C_{60}$ appears to start already at 500 K but there is no sharp decay such as that observed for the crystalline material. The amount of $N@C_{60}$ decreases rather smoothly with increasing temperature, however we could not follow this above 620 K due to technical limitations.

In the following, we discuss the origin of the enhanced thermal stability of $N@C_{60}$ inside nanotubes. It was proposed in Ref. [18] that the atomic nitrogen escapes from the fullerene cage by forming bonds with two neighboring carbon atoms from the inside and by swinging through the bonds to the outside of the fullerene. This was supported by the observation of enhanced stability of the encaged nitrogen when the fullerene was functionalized, which effectively suppresses the probability of this escape path. *Ab-initio* electronic structure calculations on the peapods indicate a hybridization of the orbitals on the fullerenes and the nanotubes [6]. Raman spectroscopy on the peapods provided experimental evidence for hybridization and a partial charge transfer between the nanotubes and the fullerenes [7]. We suggest that these effects suppress the inside-the-cage bond formation for the peapod $N@C_{60}$ similar to functionalization of the molecules.

3.2 Encapsulation of a nitroxide-fullerene spin-label As mentioned above, the yet synthesized magnetic peapods have some disadvantages. The $N@C_{60}$ is available in low concentrations and the $C_{59}N$ is an air sensitive radical. Despite these disadvantages, magnetic fullerenes are still the only known spin-labels which can

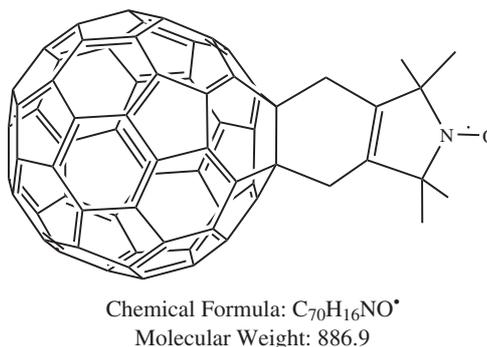


Figure 3 Schematic structure of the FCTPNO spin label molecule used for the SWCNT encapsulation. Note the presence of the pyrrolidine group with the nitroxide spin-label.

be specifically attached to the inside of the SWCNTs and which can be removed from the outside. Clearly, the ultimate SWCNT spin label is a magnetic fullerene which is available in macroscopic amounts and is not air sensitive. The above described FCTPNO molecule fulfills all these requirements and its encapsulation is reported here. The molecular structure is shown in Fig. 3, after Ref. [22]. This molecule contains a pyrrolidine-nitroxide spin label, which is very similar to the widely used TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl). We prove that the molecule is indeed encapsulated inside the SWCNTs by a control over the openings of the host SWCNTs.

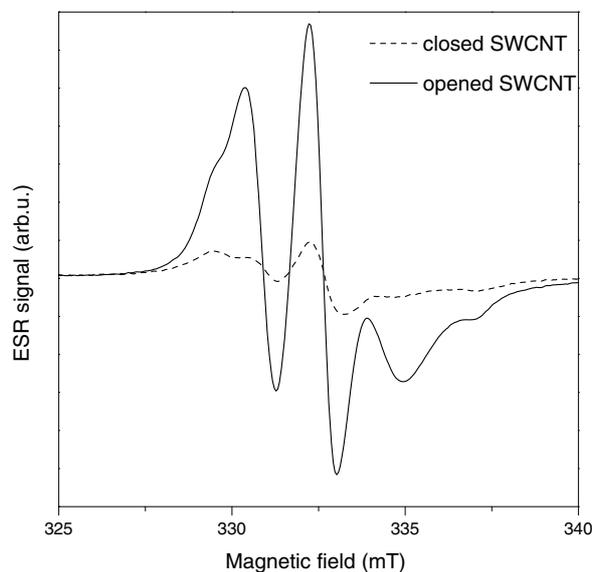


Figure 4 ESR spectra of closed and open ended SWCNTs after the solution filling process.

It is known that fullerene encapsulation requires the presence of openings on the SWCNTs [24], which can be created by acid treatment or by annealing in air. On the

contrary, openings can be closed by annealing in dynamic vacuum above 800 °C [20]. In Fig. 4. we show the ESR spectra after encapsulating the FCTPNO spin label following the standard procedure for opened and closed SWCNTs. Analysis of the ESR intensity yields the amount of encapsulated FCTPNO fullerenes. We found that the signal of FCTPNO for the closed SWCNT sample is 15 % of that in the opened SWCNTs. It means that the holes are effectively closed but some openings still remain. Nevertheless, the significant difference in the two kinds of samples (opened and closed SWCNTs) indicates that the spin-labeled fullerenes are indeed encapsulated inside the SWCNTs. In principle, Raman spectroscopy can yield the same information, however such studies have been hampered so far by the apparent light induced decay of the FCTPNO molecules.

4 Summary In summary, we studied the thermal stability of the N@C₆₀ peapods. We observed that the peapod is stable to higher temperatures than the corresponding starting crystalline material. We also presented the encapsulation of a novel type of magnetic fullerenes, a nitroxide spin labeled fullerene molecule. Independently from this work, the encapsulation of a similar nitroxide labeled fullerene was reported [25].

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