

Low temperature fullerene encapsulation in single wall carbon nanotubes: synthesis of N@C₆₀@SWCNT

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Abstract

High filling of single wall carbon nanotubes (SWCNT) with C₆₀ and C₇₀ fullerenes from solvent is reported at temperatures as low as 69 °C. A 2-h long refluxing in *n*-hexane of the mixture of the fullerene and SWCNT results in a high yield of C₆₀,C₇₀@SWCNT, fullerene peapod, material. The peapod filling is characterized by TEM, Raman and electron energy loss spectroscopy and X-ray scattering. We applied the method to synthesize the temperature sensitive (N@C₆₀:C₆₀)@SWCNT as proved by electron spin resonance spectroscopy. The solvent prepared peapod samples can be transformed to double walled nanotubes enabling a high yield and industrially scalable production of DWCNT.

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1. Introduction

Nanostructures based on carbon nanotubes [1] have been in the forefront of nanomaterial research in the last decade. Single wall carbon nanotube (SWCNT) is an even more exciting material as it represents the perfect, one-dimensional form of carbon. Fullerene encapsulating SWCNTs have attracted considerable interest after the discovery of C₆₀@SWCNT peapods [2]. More recently, several molecules have been successfully inserted into the interior of tubes such as other fullerenes, endohedral metallofullerenes or alkali halides [3]. It is believed that the inside filled structures can alter or enhance the mechanical and electronic properties of the SWCNTs or may allow the fine tuning of these parameters. However, all these synthesis methods required treatment at relatively high temperatures above 400 °C.

In particular, the peapod synthesis requires the heat treatment of SWCNT and fullerenes sealed together under vacuum, a method that appears impractical for large scale production purposes. Another important trend is the study of the behavior of the encapsulated materials under special conditions. It was recently shown that fullerene peapods are transformed into a double wall carbon nanotube (DWCNT) structure after high temperature annealing [4]. The fullerenes coalesce into an inner nanotube, which leaves the electronic properties unaffected but is expected to significantly enhance the mechanical properties of the tube system. This enhanced mechanical stability makes DWCNTs promising candidates for applications such as future electronics, probe tips for scanning probe microscopy, field emission devices and many more. Our aim in the current study was twofold: (i) development of a peapod synthesis method that allows the use of low temperatures in order to obtain encapsulated materials which do not survive the usual high temperature synthesis meth-

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ods, (ii) devising a simple method for the production of peapod starting materials to facilitate the large scale synthesis of DWCNT. In what follows, we describe the synthesis of fullerene peapods from SWCNT mixed with fullerene in solution. We present transmission electron microscopy, Raman spectroscopy, electron energy loss spectroscopy, and X-ray studies to prove that a high filling content of the peapods is achieved. We show electron spin resonance evidence that the temperature sensitive N@C₆₀ survives the filling. We also present the transformation of the solvent prepared peapod samples into DWCNT.

2. Experimental

2.1. Sample preparation

Commercial SWCNT (NCL-SWCNT from Nanocarblab, Moscow, Russia [5] and Rice-SWCNT from Tubes@Rice, Rice University, Houston, TX) and fullerenes (Hoechst AG, Frankfurt, Germany), and *n*-hexane (Merck KGaA, Darmstadt, Germany) were used for the low temperature synthesis of fullerene peapods. The NCL-SWCNT material is prepared by the arc-discharge method and is purified to 50% using repeated high temperature air and acid washing treatments by the manufacturer. The Rice SWCNT material had an initial purity of 15% and is purified with a triple repetition of H₂O₂ refluxing and HCl acid etching. The material was then filtered and degassed in dynamic vacuum at 400 °C for 1 h. The filling levels discussed below are consistent with the effective tube-end opening side-effect of the SWCNT purification [6,7]. Additional heat treatment in air or refluxing in H₂O₂ does not increase the fullerene filling levels in our samples. The mean value, d , and the variance, σ , of the tube diameters were determined from multifrequency Raman measurements [8] and it was found that $d = 1.50$ nm, $\sigma = 0.1$ nm and $d = 1.34$ nm, $\sigma = 0.09$ nm for the NCL- and purified Rice-SWCNT samples, respectively. We followed the method of Kautaura et al. [7] to fill fullerenes from the vapor phase, denoted as vapor-filling in the following. This involves sealing of the SWCNT material with the fullerene in a quartz ampoule after degassing at 300 °C and keeping it at 650 °C for 2 h. The resulting material was sonicated in toluene in order to remove non-reacted fullerenes, filtered, and dried from toluene at 400 °C in dynamic vacuum. Dynamic vacuum treatment at 700 °C is equivalent to this last step in removing non-reacted fullerene particles without an observable effect on the peapods. Fullerene filling into SWCNT in *n*-hexane, denoted as solvent-filling in the following, is achieved with mixing typically 5 mg of the SWCNT material with 10 ml *n*-hexane with 5 mg of C₆₀ or C₇₀. The as-received NCL-SWCNT materials were dried by the manufacturer and

care was taken to keep it away from humidity. The 400 °C dynamic vacuum degassing of the Rice-SWCNT was also crucial for the solvent-filling: rinsing it in water prevents any further solvent-fillability probably because water enters into the nanotubes. The SWCNT, fullerene and *n*-hexane mixture was sonicated for 5 min resulting in the partial dissolution of C₆₀ due to the relatively low room temperature solubility, 0.043 mg/ml [9], of C₆₀ in *n*-hexane. The C₆₀ solution, undissolved C₆₀ and SWCNT mixture was then refluxed at 69 °C for 2 h. After this treatment, the filtered bucky-papers were dried in air at 120 °C for 1 h. Not encapsulated C₆₀ that covers the bucky-paper is removed with the two methods mentioned above: sonication in toluene or by dynamic vacuum treatment at 700 °C. Our studies have shown that both methods yield identical materials. The same steps were followed for the production of the C₇₀@SWCNT peapod material. DWCNT transformation of the peapod samples was performed with a 2 h long dynamic vacuum treatment at 1250 °C following [4].

2.2. Transmission electron microscopy

High resolution transmission electron microscopic (HR-TEM) studies were performed on a TECNAI F20 field emission microscope equipped with a Gatan Image Filter (GIF 2001) operated at 120 or 200 kV. Electron transparent samples were prepared by drying a suspension of peapod material and *N,N*-dimethylformamide on a holey carbon grid.

2.3. Raman spectroscopy

Multi-frequency Raman spectroscopy was studied on a Dilor *xy* triple spectrometer equipped with a cryostat for the 20–600 K temperature range in the 1.83–2.54 eV (676–488 nm) energy range using an Ar–Kr mixed-gas laser. We used Raman spectroscopy to characterize the diameter distribution of the SWCNT, to determine the peapod concentration, and to monitor the DWCNT transformation of the peapod samples.

2.4. Electron energy loss spectroscopy

EELS was performed in transmission at a 170 keV in a purpose built spectrometer which combines both high energy (180 meV) and momentum resolution (0.6 nm⁻¹). Details can be found in [10] and references therein. Free standing films of about 100 nm effective thickness, which is thin enough to avoid multiple scattering, were prepared as described in [11].

2.5. X-ray studies

X-ray diffraction images were measured with Cu K α radiation from a rotating anode X-ray generator and a

pinhole camera, equipped with a two-dimensional, position-sensitive detector [12]. The system works in a 10^{-4} mbar vacuum to avoid parasitic scattering from air. Radial averages of the two-dimensional spectra were evaluated to obtain the scattering curves $q = 4\pi/\lambda \sin \theta$, with 2θ being the scattering angle and $\lambda = 0.1542$ nm being the X-ray wavelength. The strong increase in scattering intensity, that is always observed for SWCNT towards small q , is subtracted by a power-law [13].

2.6. Electron spin resonance spectroscopy

The N@C₆₀:C₆₀ endohedral fullerene:fullerene solid solution was produced in a N₂ arc-discharge tube following [14] with a typical yield of 1–10 ppm [15]. After the solvent filling steps, excess fullerenes were removed by sonication in toluene and the filtered peapod material was dried at 100 °C in air. The peapod and the reference SWCNT materials were mixed with the ESR silent high purity SnO₂ in a mortar to separate the pieces of the conducting bucky-papers. The samples were sealed under dynamic vacuum. A typical microwave power of 10 μW and 0.01 mT magnetic field modulation at ambient temperature were used for the measurements in a Bruker Elexsys X-band spectrometer.

3. Results and discussion

We performed TEM studies on our vapor and solvent prepared samples. For both kinds of materials TEM micrographs (not shown) proved that an abundant peapod concentration was achieved. However, it is not representative of the bulk of the sample thus filling efficiency has to be determined from spectroscopic investigations. In Fig. 1, we show the comparison of the Raman spectra of vapor- and solvent-filled C₆₀ peapod samples. The Raman spectra of peapod samples in the plotted frequency range consist of the SWCNT G and D modes at 1590 and 1355 cm⁻¹, respectively, and narrow lines related to the Raman active modes of the C₆₀ inside the SWCNT [7,16]. We show enlarged the most significant Raman active line of C₆₀ peapod, the A_g(2) mode. For the NCL-SWCNT peapod sample, we observe a single A_g(2) line at 1466 cm⁻¹ and for the Rice-SWCNT the well known doublet peapod signal at 1466 and 1474 cm⁻¹ [16]. The absence of an extra line at 1469 cm⁻¹, that is the Raman shift of the A_g(2) of crystalline C₆₀ and the observation of the characteristic double A_g(2) line structure in the Rice-SWCNT peapod sample are evidence that no C₆₀ is present apart from those encapsulated in the nanotubes. The larger mean tube diameter of the NCL-SWCNT is consistent with the absence of the weaker satellite of the A_g(2) at 1474 cm⁻¹ in this sample as this signal is associated with the presence of immobile C₆₀ molecules in the smaller diameter

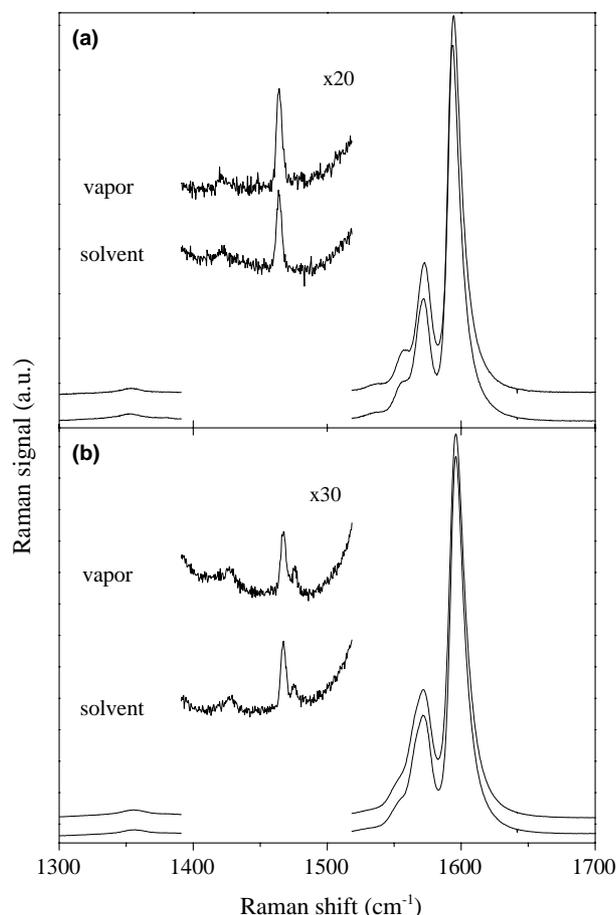


Fig. 1. (a) Raman spectra of vapor and solvent filled C₆₀@NCL-SWCNT and (b) vapor and solvent filled C₆₀@Rice-SWCNT at $\lambda = 488$ nm and 90 K. The spectra are normalized to the amplitude of the SWCNT G mode.

nanotubes [17]. We have also observed that the Raman spectra of vapor and solvent prepared C₇₀@SWCNT (spectra not shown) are also identical.

We determined the peapod concentration quantitatively from EELS measurements using the method described in [11] for both the vapor and solvent prepared samples. The C1s core level spectrum (not shown) contains contributions from carbon in C₆₀ and in the SWCNT starting material and additional carbon in the sample. When compared to a non C₆₀ encapsulating SWCNT reference, the excess C1s signal related to C₆₀ can be determined in the peapod samples. This yields the number of C₆₀ related carbon atoms that is directly translated to the filling level. Carbon in some impurity phases also affects the measurement. Thus, the values provided by this technique are only lower limits of the C₆₀ filling. Nevertheless, the current samples are of comparable quality as those in the previous study [11]. So any effect related to impurities gives the same order of error. Following [11], the C₆₀ related C1s contributions can be translated to the volume filling with simple geometrical considerations taking into account the mean

tube diameter and the 0.97 nm interfullerene distance [6]. We found that within experimental precision both the vapor and solvent prepared peapod materials have an overall C_{60} filling of $55 \pm 5\%$ for the NCL-SWCNT. This has to be compared with $61 \pm 5\%$ found in a previous study on highly filled samples prepared with the vapor method [11]. The Rice-SWCNT has a smaller peapod content as seen from the Raman spectra that is most probably related to the smaller tube diameters in this sample as C_{60} can only enter into nanotubes with $d \gtrsim 1.2$ nm [11]. Nevertheless, the similar peapod content of the vapor and solvent prepared materials emphasizes the effectiveness of the solvent filling method.

We also checked the consistency of the peapod filling content from X-ray diffraction. In Fig. 2, X-ray diffraction patterns of the pristine NCL-SWCNT, the peapod sample prepared by the vapor and the solvent method are shown. The encapsulation with C_{60} strongly modifies the intensity of the peaks, in particular the 10 peak around $q = 4.5 \text{ nm}^{-1}$ is strongly depressed in comparison to the other peaks [18]. The intensity mod-

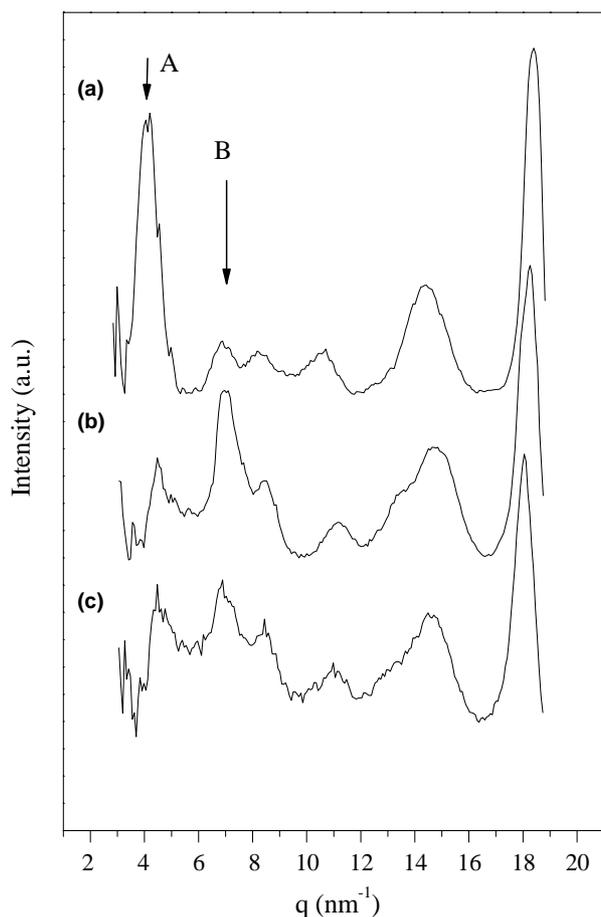


Fig. 2. X-ray diffraction profile of (a) pristine NCL-SWCNT, (b) vapor and (c) solvent prepared C_{60} @NCL-SWCNT samples. The relative intensity of the A and B peaks is a measure of the peapod concentration. The scattering peak observed at 18 nm^{-1} comes nominally from residual graphitic carbon.

ulation of the hexagonal lattice peaks by the different form factor of filled and empty SWCNT can be related to the filling content of the encapsulated peapods [18,19]. The first peak (A) decreases for filled nanotubes in comparison to the pristine SWCNT material and a second peak (B) appears, which is related to the one-dimensional lattice of the encapsulated C_{60} molecules. The X-ray spectra of the vapor and the solvent prepared peapod samples are nearly identical, which proves that a similar, high peapod filling is achieved with the two methods. Moreover, it proves that the solvent prepared peapod samples possess a similarly well ordered one-dimensional peapod structure. A numerical simulation following [18,19] leads for the inter- C_{60} distance and the coherence length of 0.95 and 25 nm, respectively, in agreement with previous electron diffraction studies [11].

In Fig. 3, we show the ESR spectra of the starting NCL-SWCNT, $(N@C_{60}:C_{60})@NCL-SWCNT$, and $N@C_{60}:C_{60}$. The ESR spectrum of the pristine NCL-SWCNT for the magnetic field range shown is dominated by a signal that is assigned to some residual carbonaceous material, probably graphite. Fig. 3c shows, that after the solvent encapsulation of $N@C_{60}:C_{60}$ in the NCL-

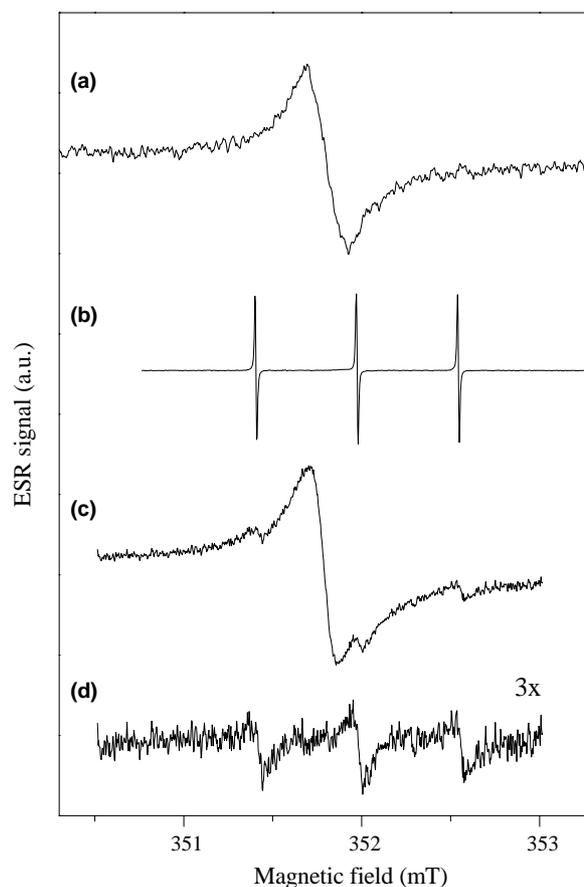


Fig. 3. X-band electron spin resonance spectrum of the (a) pristine SWCNT, (b) crystalline $N@C_{60}:C_{60}$, (c) $(N@C_{60}:C_{60})@SWCNT$ and (d) the triplet component of the $(N@C_{60}:C_{60})@SWCNT$ ESR spectrum at ambient temperature.

SWCNT, we observe a hyperfine N triplet ESR, similar to that in pristine $N@C_{60}:C_{60}$, superimposed on the broad signal present in the pristine nanotube material. Fig. 3d shows the triplet component of this signal after subtracting the signal observed in pristine SWCNT. The hyperfine triplet in $N@C_{60}:C_{60}$ is the result of the overlap of the $^4S_{3/2}$ state of the three 2p electrons of the N atom and the ^{14}N nucleus, with nuclear spin, $I = 1$. The isotropic hyperfine coupling of $N@C_{60}:C_{60}$ is unusually high as a result of the strongly compressed N atomic $2p^3$ orbitals in the C_{60} cage thus it unambiguously identifies this material [20]. The hyperfine coupling constant observed for the triplet structure in the encapsulated material, $A = 0.57 \pm 0.01$ mT, agrees within experimental precision with that observed in $N@C_{60}:C_{60}$ [20], which proves that the encapsulated material is $(N@C_{60}:C_{60})@SWCNT$. The preparation procedure, as detailed above, guarantees that non-encapsulated $N@C_{60}$ is not present in our samples. The ESR linewidth for the encapsulated material, $\Delta H_{pp} = 0.07$ mT, is significantly larger than the resolution limited $\Delta H_{pp} = 0.01$ mT in the pristine $N@C_{60}:C_{60}$ material, the lines being Lorentzian. The most probable cause for the broadening are static magnetic fields from residual magnetic impurities in the SWCNT [21]. The ESR signal intensity is proportional to the number of N spins, and this allows the quantitative comparison of N concentrations in $(N@C_{60}:C_{60})@SWCNT$ and $N@C_{60}:C_{60}$. Taking the filling value from the EELS measurement, we obtain that the N spin concentration in $(N@C_{60}:C_{60})@SWCNT$ is ~ 2.5 times smaller than in the starting $N@C_{60}:C_{60}$ material. This cannot be due to a loss of N spins during the synthesis as $N@C_{60}:C_{60}$ is stable below 100 °C and N loss becomes rapid above 220 °C only [22]. However, the observed

difference may be caused by the limited accuracy of the ESR intensity measurement also caused by microwave losses as the conducting bucky-paper pieces are separated from each-other in a poorly controlled way.

In Fig. 4, we show the Raman spectra of DWCNT prepared from vapor and solvent prepared $C_{60}@NCL$ -SWCNT peapod samples. For both spectra, the narrow Raman lines in the 250–350 cm^{-1} spectral range correspond to the inner tubes [23]. Similar patterns were observed at other laser lines (not shown) proving that the inner tube diameter distributions are identical in the two kinds of samples irrespective of the peapod synthesis method. This shows that peapod materials can be produced with the solvent method that are suitable for the production of DWCNT materials.

4. Conclusion

We presented the preparation of fullerene encapsulated SWCNT at temperatures slightly above room temperature. This method produces very high filling and provides a simple alternative to the commonly used vapor filling method. Its advantage is the relative simplicity and the possibility to scale it up to larger amounts. The mechanism by which C_{60} enters the tubes from solution at low T 's needs further exploration. At the moment, we argue that the low concentration of dissolved C_{60} in *n*-hexane behaves as a continuous source of C_{60} similar to the C_{60} vapor. The encapsulation itself is an exothermal process [25] and the loss of some degrees of freedom is compensated by the gain in potential energy. We have encapsulated a temperature-sensitive material, $N@C_{60}:C_{60}$, and observed its ESR signal. To our knowledge it is the first successful magnetic resonance experiment on an SWCNT encapsulated spin-probe. It has been speculated that such materials, when available in higher spin concentrations, may be fundamental elements of quantum-computing [24]. The solvent prepared peapod samples are transformed to DWCNT with a yield identical to that from vapor prepared materials. This opens the way for the production of high purity and highly perfect DWCNT in industrial amounts.

Note added

After preparing this manuscript for publication we learned about a similar low temperature C_{60} encapsulation method from [26] using ethanol as solvent.

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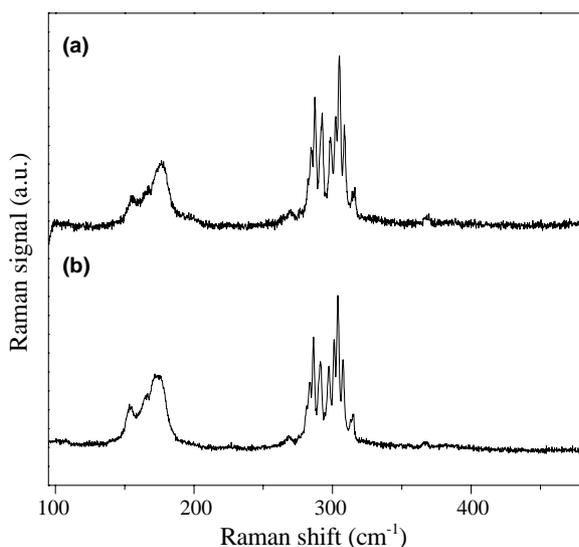


Fig. 4. Raman spectra of DWCNT obtained from (a) vapor and (b) solvent filled $C_{60}@NCL$ -SWCNT at $\lambda = 676$ nm and ambient temperature.

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