

Low-temperature encapsulation of coronene in carbon nanotubes

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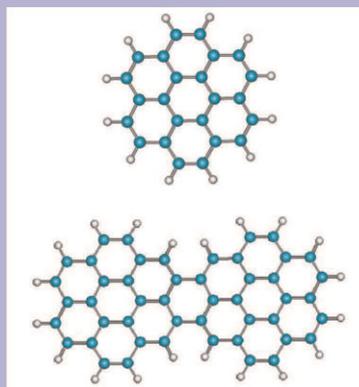
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Coronene was encapsulated in single-walled carbon nanotubes (SWNT) by vapor-phase filling at high (450 °C) and low (385 °C) temperature and by nanoextraction from supercritical carbon dioxide. The presence of coronene inside the tubes was demonstrated indirectly via the formation of double-walled nanotubes (DWNT). To this end several subsequent annealing steps were applied and monitored by Raman spectroscopy. Our results show that the encapsulation is successful with all three methods. However, high-temperature vapor filling produces adsorbed dicoronylene, the dimerized form of coronene, as a side reaction. In order to avoid dicoronylene contamination, we suggest to use low-temperature methods for the production of coronene-filled carbon nanotubes.



Coronene (top) and dicoronylene (bottom) molecules.

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1 Introduction A promising application of carbon nanotubes is their use as “nanocontainers” for various molecular species. The motivation of encapsulation can be, for example, the study of chemical reactions in a low-dimensional environment or the synthesis of new materials which, while preserving the properties of the individual constituents, become more processable and mechanically stable in the cavity of the nanotubes. Polycyclic aromatic hydrocarbons have evoked considerable attention lately in both areas. It was attempted to preserve their molecular fluorescence [1] or to subject them to polymerization reactions resulting in graphene nanoribbons [2].

In the coronene-filled nanotubes first prepared by Okazaki et al. [1], stacked columns of coronene molecules

inside the nanotubes were imaged by high-resolution transmission electron microscopy (HR-TEM). Talyzin et al. [2] likewise, obtained HR-TEM images showing the coalescence of the molecules into graphene nanoribbons at elevated reaction temperatures. Besides HR-TEM, an alternative (although destructive) bulk method can be used to demonstrate the encapsulation. For this purpose, the filled single-walled carbon nanotubes (SWNT) are annealed at high temperature to convert the enclosed molecules into inner nanotubes and thus form double-walled nanotubes (DWNT) [3]. This method can also differentiate between encapsulated species and those adsorbed on the outer surface. Such transformations have been studied successfully on

fullerene-containing nanotubes (peapods) by the combination of various spectroscopic methods [4, 5]. Similarly, the annealing of ferrocene-filled SWNT also resulted in DWNT formation [6]. Very recently it was reported that heating of nanotubes containing polyaromatic hydrocarbons, such as perylene or coronene, will produce similar results [7].

Here we present alternative techniques for coronene encapsulation with particular regard to the effect of the encapsulation temperature on the product. The presence of coronene inside the nanotubes is proven by transforming them into DWNT and identifying the inner tubes by Raman spectroscopy [8]. Our results show that all samples are filled. The high-temperature sublimation process, however, also produces dicoronylene, adsorbed on the surface of the nanotubes.

2 Experimental Three different samples were prepared: (i) vapor phase filling at high temperature, (ii) vapor phase filling at lower temperature, and (iii) nanoextraction [9–11] using supercritical CO₂. For reference and starting material, P2 SWNTs (Carbon Solutions, diameter range: 1.2–1.6 nm [12]) were used. Before filling, the starting material was opened by annealing at 570 °C in air for 20 min. Vapor filling was performed at 450 °C (“high temperature”) and 385 °C (“low temperature”) using the method described by Okazaki et al. At low temperature dimerization of coronene molecules could be avoided. (Coronene sublimates above 325 °C at 10⁻⁴ mbar.) The nanoextraction [13] was performed in a closed high pressure reactor [4] under supercritical CO₂ at 50 °C and 150 bar for 96 h. Each sample was repeatedly washed with toluene to remove excess coronene from the exterior of the tubes, until the solution contained <0.001 mg ml⁻¹ coronene. The washing process was monitored by UV–visible and/or photoluminescence spectroscopy. The encapsulated species were converted into DWNT by annealing at 1250 °C for 24 h in evacuated sealed quartz capsules. In all cases, pristine SWNT were used as reference; this sample underwent the same annealing sequence without adding coronene.

The reference SWNT, the samples with encapsulated coronene and the DWNT were characterized by Raman microscopy. Data were acquired in backscattering geometry under ambient conditions. The laser power was carefully adjusted to avoid any type of changes in the samples. Spectra were taken by using four excitation wavelengths with three different spectrometers: a Renishaw 1000B with a 785 nm diode laser line, a Jobin-Yvon T64000 with a 482 and a 531 nm Kr⁺ line and an FT-Raman module connected to a Bruker IFS 55v spectrometer with a 1064 nm diode-pumped Nd:YAG laser line.

3 Results and discussion In Fig. 1, we show the Raman spectra of the samples after the encapsulation reaction. Independent of the excitation energy, no additional Raman lines are observed in the samples prepared with low-temperature sublimation and nanoextraction. Figure 2

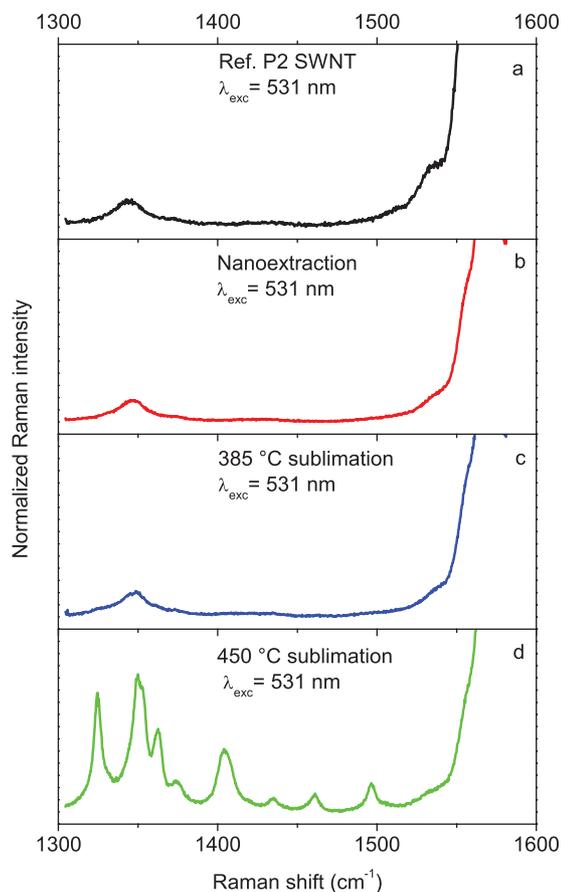


Figure 1 (online color at: www.pss-b.com) Raman spectra in the range of the G-mode after different filling procedures. Shown are only spectra measured at $\lambda_{\text{exc}} = 531$ nm. (a) Reference P2 SWNT. Coronene@SWNT using (b) nanoextraction, (c) low-temperature sublimation, (d) high-temperature sublimation. The intensities have been normalized to that of the G peak.

compares the Raman spectra of the reference SWNT, of coronene and dicoronylene with the sample filled at high temperature. Since the scattering from encapsulated molecules is notoriously weak and since the strongest coronene and dicoronylene Raman modes coincide with the D- and G-mode of the nanotubes, the observation of encapsulated molecules is difficult. Nevertheless, in the material prepared at high temperature dicoronylene lines appear with considerable intensity (Fig. 2d). We assign these lines to dicoronylene adsorbed on the nanotubes by π - π stacking. This interaction and the insolubility of dicoronylene in most solvents makes it difficult to remove it either by sublimation or by washing.

Since the direct Raman characterization of the encapsulated molecules is not trivial in the presence of adsorbed species, we produced DWNT from all samples by annealing. After annealing, new radial breathing modes (RBM) at higher energies are present for all filling techniques (Fig. 3), indicating the appearance of nanotubes with diameters smaller than those of the reference SWNT [14]. The

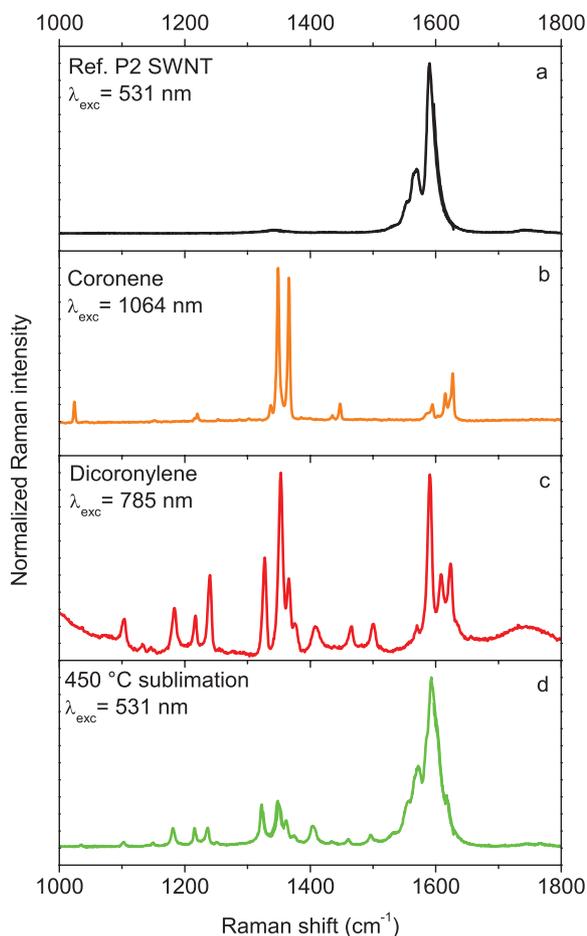


Figure 2 (online color at: www.pss-b.com) Raman spectra of (a) the starting P2 SWNT, (b) coronene, (c) dicoronylene, and (d) coronene@SWNT filled by high-temperature sublimation. The excitation lines are indicated.

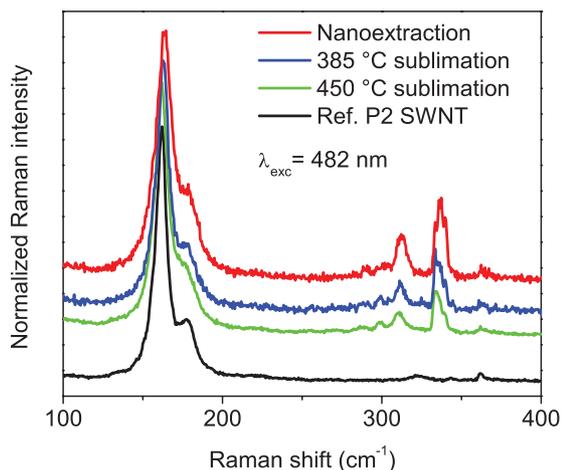


Figure 3 (online color at: www.pss-b.com) Raman spectra in the RBM range after annealing at 1250 °C. From bottom to top: reference SWNT, coronene@SWNT using high- and low-temperature sublimation and nanoextraction. The spectra have been normalized to the intensity of the G-mode and are offset for clarity.

positions of the new lines coincide with those measured earlier on fullerene-based peapods [5]. The inner tube RBM structure consists of more modes than expected from the number of geometrically allowed modes and it results from the van der Waals interaction between the inner and outer walls [15, 16]. Thus, encapsulation can be pinpointed by this indirect procedure of DWNT formation. The exact nature of the encapsulated species does not follow from these results and has to await HR-TEM investigations; according to Talyzin et al. [2] the samples filled at high temperature contain oligomers of coronene, while the low-temperature methods may yield nanotubes filled with individual coronene molecules.

4 Conclusions We found that coronene can be encapsulated in SWNT by vapor phase filling at lower temperature than previously employed [1, 2], and nanoextraction from supercritical CO₂ as well. A side product of high-temperature vapor filling is dicoronylene adsorbed on the outer walls of nanotubes, and it cannot be removed by standard purification techniques. Double-walled nanotubes could be formed from all samples and proved the success of the filling. The chemical nature of the encapsulated species could not be determined exactly; based on the lack of external dicoronylene in the samples prepared at low temperature, we suggest that these contain monomeric coronene molecules in contrast to oligomers or polymers in materials annealed above 420 °C.

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