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The Change of the State of an Endohedral Fullerene by Encapsulation into SWCNT: A Raman Spectroelectrochemical Study of $Dy_3N@C_{80}$ Peapods

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Abstract: Raman and in situ Raman spectroelectrochemical studies of $Dy_3N@C_{80}$@SWCNT peapods have been carried out for the first time. The formation of peapods by the encapsulation of gaseous $Dy_3N@C_{80}$ has been confirmed by HR-TEM microscopy and by the successful transformation of $Dy_3N@C_{80}$@SWCNT into double-walled carbon nanotubes. The Raman spectra of the endohedral fullerene cluster changed dramatically in the interior of the single-walled carbon nanotube (SWCNT). The electrochemical charging of the peapod indicates a slight reversible attenuation of the Raman intensities of fullerene features during anodic doping. The results support the assignment of Raman bands to the $Dy_3N@C_{80}$ moiety inside a SWCNT.

Keywords: dysprosium · electrochemistry · fullerenes · nanotubes · Raman spectroscopy

Introduction

Among the endohedral metallofullerenes, trimetallic nitride fullerene clusters are distinguished by their outstanding high-yield syntheses compared to those achieved for empty fullerenes and conventional mono- and dimetallofullerenes, their high thermal stability, and their long-term stability in air.[1,2,3] Among the new fullerene clusters recently synthesized through variation of the trapped clusters, the C_{80} fullerenes are the most prominent cages in accommodating these species.

Current efforts in the field of carbon nanostructures have lead to the synthesis of a new class of materials called fullerene peapods. These materials consist of single-walled carbon nanotubes (SWCNTs) filled with fullerenes, the generic structure being C_{60}@SWCNT.[4] Filling the SWCNT with endohedral fullerenes has also been demonstrated.[5,6] These new materials can be used in the engineering of field effect transistors (FET) with a controlled energy gap by varying the metallofullerenes encapsulated in the SWCNT.[7–9] Therefore, the study of the electronic structure of this new class of materials is essential in understanding their properties. In situ spectroelectrochemistry has been shown to be the method of choice to study the electronic properties of carbon nanostructures.[10–13] Recently, we successfully produced a high yield of $Dy_3N@C_{80}$ using a modified Krätschmer–Huffman DC-arc discharging method.[14,15] Due to the high stability of this material, it was a challenge to use it as a precursor for the preparation of peapods.[16]

The research on peapods of endohedral fullerenes is mainly based on high-resolution transmission electron microscopy (HR-TEM). This method can provide direct evidence for the formation of the peapod. However, as only a small part of the sample can be analyzed by HR-TEM, the data provided by this method are generally not representative of the bulk sample. Furthermore, this method is not suitable for investigations of the electronic structure. Employing X-ray photoelectron spectroscopy (XPS), we have demonstrated the existence of a charge transfer between $Dy_3N@C_{80}$ and SWCNTs.[16,17] The electronic structure of the

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peapods can be studied by Raman spectroscopy as was shown for C_{60}@SWCNT and C_{70}@SWCNT peapods.[10,12] Except for a few studies, the results of which are contradictory, almost no Raman data on other fullerene peapods exist. The Raman studies of La_2@C_{80}@SWCNT[18] and Ti_2@C_{80}@SWCNT[19] indicate unexpectedly high intensities of the intratubular fullerene bands, which were even stronger than the SWCNT bands. This behavior was explained by a so-called "antenna effect".[19] However, as the fullerene bands can overlap the Raman features of the metal oxides used for the synthesis of endohedral fullerene, one can mismatch the fullerene features with those of metal oxide impurities. On the other hand, Ohno et al.[20] did not observe a fullerene band for Gd@C_{82}@SWCNT in the low frequency region at which the radial breathing modes (RBM) of SWCNT also occur. An indication of peapod existence was a small shift of the RBM in the Raman spectra.[20]

In this study, we present the first Raman spectroscopic and in situ Raman spectroelectrochemical study results on the endohedral cluster fullerene peapod Dy_3N@C_{80}@SWCNT. Our data differ qualitatively from previous Raman spectroscopic studies on La_2@C_{80}@SWCNT[18] and Ti_2@C_{80}@SWCNT.[19] We have found new features at frequencies close to the tangential displacement (TG) mode region, but fullerene bands were not detected in the RBM region.

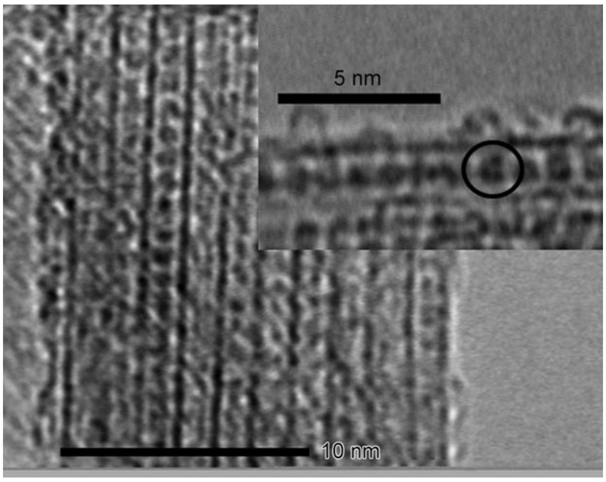

Figure 1. HR-TEM image of Dy_3N@C_{80}@SWCNT. The inset shows a close-up with one encapsulated Dy_3N@C_{80} marked by a circle. The dark spots can be attributed to Dy and indicate that the intratubular fullerene encages three atoms of Dy.

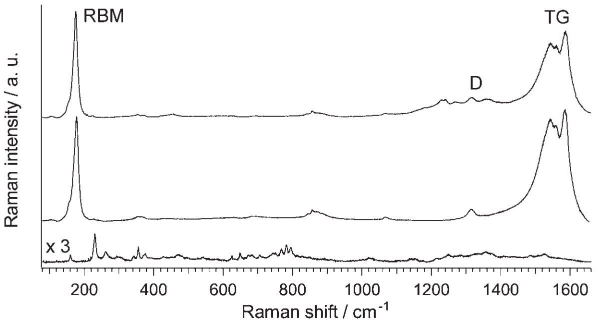

Figure 2. Raman spectra recorded at the 1.83 eV laser excitation energy. From top to bottom: Dy_3N@C_{80}@SWCNT, SWCNT, and Dy_3N@C_{80}. The spectra are offset for clarity. The intensity scale is identical for the top two plots, and it is increased by a factor of 3 for the last plot, as indicated.

Results and Discussion

Peapod formation: The Dy_3N@C_{80}@SWCNT has recently been prepared in vacuo by a temperature "shock" treatment of the Dy_3N@C_{80} film evaporated onto SWCNT.[16] Here, we present another possibility for the Dy_3N@C_{80}@SWCNT preparation: the long-term heat treatment of Dy_3N@C_{80} with SWCNT at temperatures slightly above the sublimation point of fullerene. This procedure was used previously for the preparation of peapods from other endohedral fullerenes.[6,21,22]

Figure 1 shows the HR-TEM picture of this prepared Dy_3N@C_{80}@SWCNT peapod. The fullerene cluster molecules are confirmed to be encapsulated inside the SWCNT and form a one-dimensional array with a regular center-to-center distance of about 1.1–1.2 nm. Three separated regions of dark contrast attributed to Dy atoms are detected in the fullerene cluster molecules; this fact unambiguously indicates the existence of the fullerenes inside SWCNT encaging three atoms of Dy. The TEM picture confirms the triangular shape of the Dy_3N cluster in the Dy_3N@C_{80},[23] which is preserved after encapsulation of the fullerene into the SWCNT.

Figures 2 and 3 show the Raman spectra of Dy_3N@C_{80}@SWCNT peapods, pristine SWCNT, and Dy_3N@C_{80} excited by a laser photon energy of 1.83 and 1.91 eV, respectively. The diameter distribution of the SWCNT is critical for their filling with fullerenes. The optimum diameter for encapsulation of Dy_3N@C_{80} is expected to be between 1.4 and 1.5 nm. The found RBM frequency of 167 cm^{-1} (at the 1.91 eV excitation) translates according to a well-known dependence [Eq. (1), see reference [24]] into a diameter of 1.44 nm.

$$d = 217.8/(\omega\text{-}15.7) \tag{1}$$

This is close to the optimum diameter for fullerene encapsulation and makes our SWCNT sample a good candidate for high-yield filling. Nevertheless, it should be noted that only the SWCNTs that fulfill the resonance condition are visible in the Raman spectra. Furthermore, in dry samples, nanotubes are packed in a tight bundle (of antennas) that can significantly change the position of the RBM mode. Hence, the maximum of the resulting envelope of Raman scattering is not directly related to the average diameter. Thus, the value of 1.44 nm can be considered only as a rough estimate.

As shown in Figure 3, there is an upshift of the RBM in Dy_3N@C_{80}@SWCNT relative to that found for pristine SWCNTs. For isolated tubes/peapods, the change in the

RBM position is believed to indicate the encapsulation of the fullerene cluster inside the SWCNT.[20] However, in our case, the RBM band is a superposition of several Raman lines. Heat treatment can change the nanotube agglomeration, so the nanotube optical absorption bands may be shifted. The shift of the optical absorption bands would cause changes in the resonance conditions for individual tubes, thus influencing the weights of their RBM lines in the Raman spectra. Therefore, the overall shift of the RBM alone is not reliable evidence for filling.

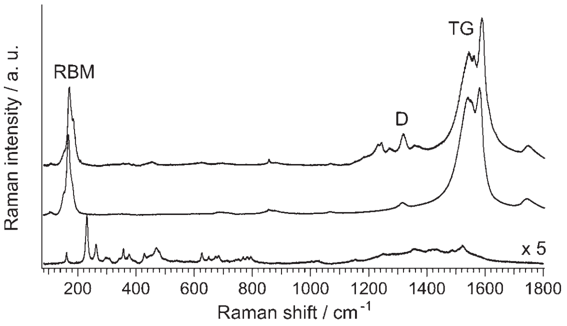

Figure 3. Raman spectra recorded at the 1.91 eV laser excitation energy. From top to bottom: $Dy_3N@C_{80}$@SWCNT, SWCNT, and $Dy_3N@C_{80}$. The spectra are offset for clarity. The intensity scale is identical for the top two plots and is increased by a factor of 5 for the last plot as indicated.

The TG mode also has a slight upshift. This indicates a charge transfer from the encapsulated fullerene cage to the SWCNT. The upshift of the TG mode is usually attributed to p-doping, as previously shown for electrochemical doping.[10,25,26] The C_{80} cage is believed to carry up to six extra electrons transferred from the Dy_3N cluster in $Dy_3N@C_{80}$. Nevertheless, experimental data has shown that the oxidation state of Dy is slightly reduced to a value of 2.8, resulting in a total charge on the cluster of 5.4.[17] As we have previously shown by using photoelectron spectroscopy, the formation of a peapod leads to a change in the effective Dy oxidation state to about 3.0.[16] Thus, our recent Raman data agree with the data obtained by photoelectron spectroscopy.

The Raman bands assigned to the fullerene cluster changed drastically upon its encapsulation into the SWCNT. Five bands between 1100 and 1450 cm^{-1} were found in the spectra of the $Dy_3N@C_{80}$@SWCNT peapod: 1182, 1230, 1245 and 1360 cm^{-1} and were assigned to the encapsulated $Dy_3N@C_{80}$. (The band at 1320 cm^{-1} corresponds to the D-mode of pristine SWCNT; therefore, we suggest the same assignment for $Dy_3N@C_{80}$@SWCNT.) The Raman spectra in the TG region of $Dy_3N@C_{80}$ are very complex. There are many overlapping bands that are difficult to resolve. Thus, it is impossible to follow the changes of the individual bands in this region upon encapsulation of $Dy_3N@C_{80}$ into the SWCNT. Nevertheless, it is clear that the shape of the spectral envelope has changed upon encapsulation. The reason could be an activation of the IR modes that are relatively strong in the 1100–1600 cm^{-1} region.[23]

Surprisingly, no bands arising from the fullerene cluster were found below 1100 cm^{-1} in the Raman spectra of the $Dy_3N@C_{80}$@SWCNT peapod. They are either missing or overlapped by SWCNT features. This is in contrast with the spectra of peapods containing empty fullerenes, for example, C_{70}@SWCNT or C_{60}@SWCNT, in which only slight changes in the fullerene band positions are observed.[27]

The marked differences at low frequencies between the spectra of a free $Dy_3N@C_{80}$ fullerene and that after insertion into the SWCNT are not yet understood. The possible polymerization of fullerenes could be responsible for the lowering of the symmetry, leading to a broadening and splitting of the bands. However, the $Dy_3N@C_{80}$ fullerene is very stable and thus its polymerization is not very probable at the conditions used. The electronic structure of the free and of the encapsulated $Dy_3N@C_{80}$ could be different due to the interaction of the fullerene cage with the carbon nanotube. A charge transfer from the $Dy_3N@C_{80}$ fullerene to the SWCNTs wall could change the resonance condition. Thus, the resonance enhancement could be erased for particular modes, and some other modes could increase in intensity. Such a dramatic change was not observed for C_{60}@SWCNT or for C_{70}@SWCNT; however, the uncharged C_{60} and C_{70} fullerenes exhibited resonantly enhanced Raman spectra for the excitation photon energy of about 2.4–2.6 eV. Thus, predominately semiconducting SWCNT are resonantly enhanced simultaneously with the spectra of C_{60} and C_{70} fullerenes. For higher cages, the resonant condition is shifted to the red region of about 1.9 eV at which the metallic tubes are resonantly enhanced. As shown before, a strong electron phonon coupling in metallic tubes exists; hence, the carbon nanotube could be less transparent for red light. Another reason could be the broadening of the fullerene's RBM due to the non-spherical shape of the $Dy_3N@C_{80}$ cage and/or due to interactions between the C_{80} cage and tubes of different diameters.

Despite careful purification of the SWCNT sample, it may still contain traces of amorphous carbon. (The Vis/NIR spectra of the starting SWCNT suspended in a solution of 0.8% (wt) SDS (sodium dodecyl sulfate) in D_2O are shown

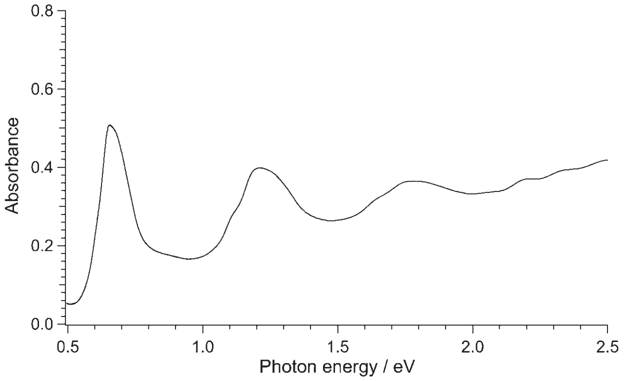

Figure 4. Vis/NIR spectra of the SWCNT starting material used for $Dy_3N@C_{80}$@SWCNT preparation. The spectra were measured in a solution of 0.8% (wt) SDS in D_2O.

in Figure 4.) Amorphous carbon is chemically more active than the nanotubes themselves. So, $Dy_3N@C_{80}$ could react with amorphous carbon to produce new substances. The quality of the nanotube sample is critical for the success of filling, which in turn can be used as an indication of the quality of the carbon nanotubes. The same SWCNT sample was used to prepare the C_{70} and C_{60} peapods. The spectra of the resulting materials exhibited only slightly modified bands of the starting fullerenes (not shown). If the SWCNT sample had contained reactive impurities, they should have also reacted with C_{60} or C_{70}, but no dramatic change as in case of $Dy_3N@C_{80}$ peapods was found.

To demonstrate that the Raman spectra did not result from unreacted or partially decomposed $Dy_3N@C_{80}$ fullerenes outside the tube, the following experiments were carried out. First, a sample of $Dy_3N@C_{80}$@SWCNT was sonicated for 60 min in an excess of toluene, in which $Dy_3N@C_{80}$ is soluble, then filtered and measured. No change in the Raman spectra of the $Dy_3N@C_{80}$@SWCNT before and after this treatment was observed. Second, the etching of the $Dy_3N@C_{80}$@SWCNT material was tested. The sample was sonicated for approximately 10 min in 68% HNO_3 at 70°C. This procedure resulted in a loss of about 75% of the material's total amount. The spectra (not shown) of the remaining sample exhibited a decrease in the intensity of the SWCNT modes. The D-line in the spectra of the sample after etching was slightly increased, indicating new defects that could reduce the signal of the SWCNT. The treatment of SWCNT in HNO_3 is known to result in the doping of the sample.[28] The doping causes a loss in resonance in Raman spectra by quenching the optical transitions (in our case: E_{11}^{M}), which explains the bleaching of tube modes. On the other hand, the intensity of other bands assigned to $Dy_3N@C_{80}$ at 1182, 1230, 1245 and 1360 cm^{-1} was not affected. This important result confirms that the species responsible for the signal is neither etched nor doped. It supports our assumption that the new bands originated from intratubular $Dy_3N@C_{80}$. In addition, we performed a test using a C_{60}@SWCNT sample. The etching of the sample led to a slight enhancement of the C_{60}-related $A_g(2)$ mode signal, confirming our conclusions.

The C_{60}@SWCNT or C_{70}@SWCNT peapods can be transformed into double-walled carbon nanotubes (DWCNTs) as previously demonstrated.[29] Such a transformation can be used as an indirect proof of the presence of peapods in the material being studied. It has been suggested that the same should be valid for peapods containing fullerene clusters. Indeed, heating $Dy_3N@C_{80}$@SWCNT led to the formation of DWCNT indicated by Raman spectra (Figure 5). Furthermore, the features that were assigned to $Dy_3N@C_{80}$ in the $Dy_3N@C_{80}$@SWCNT peapods are completely absent in the spectra of the sample after the pyrolytic conversion. Note that the diameter distribution of the inner tubes in the DWCNT prepared from $Dy_3N@C_{80}$@SWCNT were slightly different than those of the DWCNT prepared from C_{60}@SWCNT or C_{70}@SWCNT fullerene peapods. The intensity of the signal of the inner tubes at high frequencies is considerably lower for DWCNT prepared from $Dy_3N@C_{80}$@SWCNT than those prepared from C_{60}@SWCNT or C_{70}@SWCNT fullerene peapods. Evidently, the formation of inner tubes with a narrower diameter was hindered for the $Dy_3N@C_{80}$@SWCNT. Assuming the ideal diameter for filling of SWCNT with $Dy_3N@C_{80}$ to be 1.45 nm and 0.34 nm an ideal distance between the inner and the outer tube, the diameter of inner tubes should be about 0.77 nm, which corresponds to a RBM position at approximately 300 cm^{-1}. According to the Kataura plot, the 0.77 nm diameter tubes are in resonance with a laser energy of about 1.8 eV. (It is important to note that the Raman spectra of DWCNT do not necessarily display the corresponding inner and outer tubes in the same laser excitation.) Hence, using a laser energy of 1.83 eV, the inner tubes with the "optimum diameter" are expected to be in resonance, whereas the 1.91 eV excitation should lead to the resonance of the inner tubes with a smaller than optimum diameter; the intensity of these bands was considerably smaller. We believe that the formation of thinner tubes is not preferable due to the presence of metal clusters in the fullerene. Thus, the endohedral Dy_3N cluster influences the final diameter of inner tubes in the DWCNT grown from $Dy_3N@C_{80}$@SWCNT. The major effect seems to be the steric prevention of the formation of narrow-diameter tubes. The formation of wider, inner tubes can also be related to the larger diameter of C_{80} with respect to C_{70} or C_{60}.

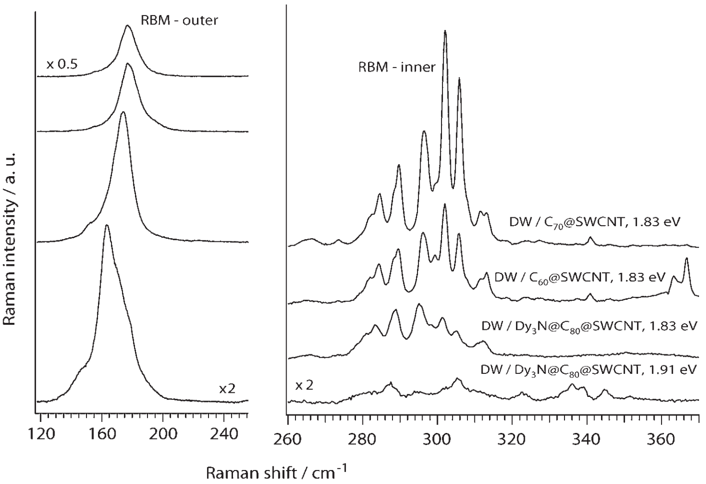

Figure 5. Raman spectra of DW/C_{70}@SWCNT, DW/C_{60}@SWCNT, and DW/$Dy_3N@C_{80}$@SWCNT. The spectra are offset for clarity. The respective intensity scales are identical for all plots except the left top, left bottom, and right bottom plots (with scaling factors of 0.5, 2, and 2, respectively, as indicated).

In situ spectroelectrochemistry of $Dy_3N@C_{80}$@SWCNT: The potential-dependent Raman spectra (excited at 1.91 eV) of $Dy_3N@C_{80}$@SWCNT in an acetonitrile electrolyte solution are shown in Figure 6. The electrochemical charging, both cathodic and anodic, caused the bleaching of both RBM and TG modes (not shown). A second distinctive effect was the blue shift of the TG mode upon anodic charging. The effect of attenuation of Raman spectra of tube-related modes by

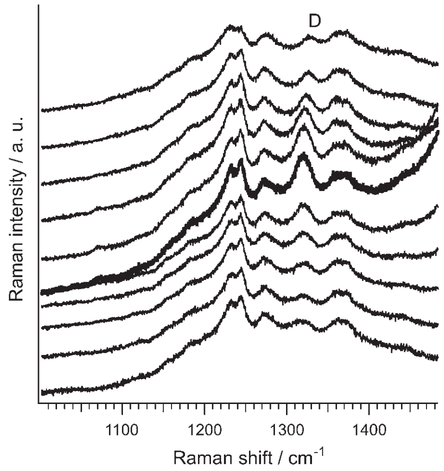

Figure 6. Potential dependent Raman spectra (excited at 1.91 eV) of $Dy_3N@C_{80}@SWCNT$ on a Pt electrode in 0.2 M $LiClO_4$ + acetonitrile. The electrode potential was varied by steps of 0.3 V from 1.2 to −1.8 V vs. Fc/Fc^+ for the curves from top to bottom. The bold curve belongs to a spectrum recorded at a potential close to the open circuit value. Spectra are offset for clarity, but the intensity scale is identical for all spectra.

electrochemical charging has already been described[25,26,30] and is attributed to the disappearance of the resonance enhancement due to the filling (depletion) of van Hove singularities by the electrochemical charging. For Raman excitation at 1.91 eV, the loss of resonance is caused by a quenching of the optical transitions E_{11}^{M}. Consequently, the charging also erases the Fano broadening in outer metallic tubes at both cathodic and anodic potentials.[31] The blue shift of the TG mode upon anodic charging reflects the stiffening of the graphene mode if holes are introduced into the π band.[32,33] These effects are similar for both filled (represented by $Dy_3N@C_{80}@SWCNT$) and empty SWCNTs.

In the region of 1100–1400 cm^{-1}, the band at 1320 cm^{-1} is the one most sensitive to electrochemical charging. This band corresponds to the position of the D-mode of the SWCNT and has also been assigned to the D-mode of $Dy_3N@C_{80}@SWCNT$.[26] As expected, the bleaching of this band is roughly symmetrical for anodic and cathodic charging. Furthermore, the expected slight upshift of this band in the case of an anodic charging and a downshift during cathodic charging correspond well with our measurements (Figure 6).

The remaining bands between 1100–1400 cm^{-1} exhibited only a weak dependence on the applied electrochemical potential. A small decrease in the intensity of the double band centered at 1240 cm^{-1} was seen during the anodic doping, but no significant bleaching was observed during cathodic doping. The bleaching of the bands was reversible. Furthermore, this confirms that the $Dy_3N@C_{80}$ fullerene was encapsulated inside the SWCNT. The in situ spectroelectrochemistry shows that the charging of the tube's outer surface influences the species in the interior. Usually the encapsulated species exhibits a somewhat delayed but traceable attenuation of the intensity of Raman modes, for example, the inner tubes in the DWCNT,[26,31] C_{70} in $C_{70}@SWCNT$,[10] and C_{60} in potassium-doped $C_{60}@SWCNT$.[12] The spectroelectrochemical test can be very useful to distinguish species both out- and inside SWCNTs. For example, the unprotected C_{60} is irreversibly oxidized by applying an anodic potential and the Raman signal is progressively bleached. On the other hand, if the C_{60} is protected inside a nanotube, the signal of C_{60} in a peapod increases as a result of the so-called "anodic Raman enhancement",[10] an unambiguous indication that C_{60} is inside the SWCNT. The anodic enhancement does not apply for C_{70} peapods, thus the effect cannot be generalized.[10] In the case of C_{70} peapods, the signal is only slightly bleached and is recovered upon going back to a potential of 0 V. This again points to C_{70} encapsulated in the SWCNT. For $Dy_3N@C_{80}@SWCNT$, we also observed a reversible change in the intensity. We assume this is an indication of encapsulated $Dy_3N@C_{80}$. We also believe that the strength of the electronic coupling has an effect on the bleaching. Considering simple electrostatic interactions of $Dy_3N@C_{80}$ and SWCNTs, the anodic doping should strengthen the interactions between the negatively polarized fullerene cluster cage and the outer tube, which is p-doped. The stronger the interaction, the stronger is the change in the electronic structure of the encapsulated $Dy_3N@C_{80}$ which can weaken the resonance effect. This is in agreement with the observed Raman spectra. Furthermore, the bleaching of fullerene cluster bands during p-doping is reminiscent the spectroelectrochemical study of potassium-doped C_{60}-peapods, which were subsequently electrochemically p-doped.[12] In the latter case, the C_{60} molecule carried four electrons, leading to a bleaching of the $A_g(2)$ mode during electrochemical anodic charging and remaining almost unchanged during electrochemical cathodic doping. Recent data obtained by photoelectron spectroscopy on $Dy_3N@C_{80}$ proved that each Dy ion has a oxidation state of 2.8, indicating a charge transfer between the dysprosium cluster and the fullerene cage.[17] Therefore, the cluster–cage bonds are strongly polarized and some similarities with the case of potassium-doped C_{60} peapods are expected. Nevertheless, we should note that the situation of $Dy_3N@C_{80}@SWCNT$ is not identical to that for potassium-doped C_{60}-peapods, since the C_{60} anion is formed in these peapods, whereas the fullerene cluster $Dy_3N@C_{80}$ is polar but neutral. Furthermore, the position of the metal counterion is different. For potassium-doped peapods, the metal counterion is outside of the cage, while in $Dy_3N@C_{80}@SWCNT$ it is inside. Thus, the analogy in the behavior of endohedral ($Dy_3N@C_{80}@SWCNT$) and exohedral (K-doped $C_{60}@SWCNT$) peapods during electrochemical doping must be used with caution. The qualitatively different localization of the metal atom can be responsible for the extension of the effect.

The bleaching of the bands of encapsulated $Dy_3N@C_{80}$ is only slight, even during anodic charging. This might point to a relatively weak electronic contact between the encapsulated fullerene cluster and the SWCNT. The depleted electronic states of the tube can serve as an alternative explanation for the observed effect. The anodic charging leads to a withdrawal of electrons from the tube and might cause a better transparency of the tube wall. The so-called "anodic enhancement" of the fullerene signal could therefore apply as for C_{60} peapods.[10] Thus, the electronic contact between the tube and the fullerene can indeed be strong, but the bleaching of the fullerene bands is "reduced" by anodic enhancement of the fullerene bands.

Conclusion

Here we have presented a Raman spectroscopic and an in situ Raman spectroelectrochemical study of $Dy_3N@C_{80}@$SWCNT peapods. The formation of peapods has been confirmed by HR-TEM. The resulting $Dy_3N@C_{80}@$SWCNT peapods were successfully transformed into DWCNTs. The insertion of $Dy_3N@C_{80}$ into SWCNTs caused a change in the $Dy_3N@C_{80}$ bands in the Raman spectra of the resulting material. The bands assigned to encapsulated $Dy_3N@C_{80}$ persisted after intensive washing with toluene and even after etching with 68% HNO_3. Therefore, the bands correspond to a species inside the SWCNTs. The bands assigned to $Dy_3N@C_{80}$ inside the SWCNTs are reversibly bleached by an anodic electrode potential. This is further evidence of the presence of $Dy_3N@C_{80}$ inside the SWCNTs.

Experimental Section

The trimetal nitride fullerene cluster $Dy_3N@C_{80}$ was produced by a modified Krätschmer–Huffman arc discharge method.[2] Fullerenes were isolated and identified by high-performance liquid chromatography (HPLC), vibrational spectroscopy, and by laser desorption time-of-flight mass spectrometry.[14]

The peapods were synthesized by using SWCNTs available from our previous work.[10] The SWCNTs were prepared by laser ablation[34] and purified by reflux in 15% H_2O_2. This was followed by washing with HCl to remove residual catalyst.[35] The purified SWCNTs were opened by treatment at 450°C for 30 min in air. The $Dy_3N@C_{80}@$SWCNT peapods were prepared by heating $Dy_3N@C_{80}$ with SWCNTs sealed in an evacuated quartz ampoule at 550°C for 3 d. The sample was then heated at 550°C for 6 h in vacuo to remove the residual $Dy_3N@C_{80}$.

Double-walled carbon nanotubes (DWCNTs) were prepared by a pyrolysis of the $Dy_3N@C_{80}@$SWCNT peapods. The conversion was carried out at 1200°C under vacuum; the length of heating was 8 h.

The HR-TEM measurements were performed by using a Philips CM 200 at an acceleration voltage of 200 kV with a LaB_6 filament source.

The $Dy_3N@C_{80}@$SWCNT-coated electrodes for in situ spectroelectrochemical studies were produced by evaporation of a sonicated ethanol slurry of peapods on a Pt electrode. The film was outgassed at 80°C in vacuo. Then, the particular electrode was mounted into the air-tight, one-compartment Raman spectroelectrochemical cell equipped with glass optical window for spectroscopic measurements.

The cell was assembled in a glove box (M. Braun). The box's atmosphere was N_2 and contained <1 ppm of both O_2 and H_2O. Electrochemical experiments were carried out by using a PG 300 (HEKA) or a 273 A (EG&G PAR) potentiostats. The electrochemical cell contained Pt auxiliary and Ag-wire pseudo-reference electrodes. The electrolyte solution was 0.2 M $LiClO_4$ + acetonitrile (both from Aldrich; dried over 4 Å molecular sieve). After each set of spectroelectrochemical measurements, ferrocene (Fc) was added to the cell to measure the redox potential of the Fc/Fc^+. The potentials measured against the Ag pseudoreference electrode were recalculated and related to the Fc/Fc^+ couple.

The Vis/NIR spectra were recorded on a UV/Vis/NIR 3101-PC spectrometer (Shimadzu, Japan). The Raman scattering was excited by a Kr^+ laser at 1.83 and 1.91 eV (both from the Innova 300 series, Coherent). Spectra were recorded on a T-64000 spectrometer (Jobin Yvon) interfaced to an Olympus BH2 microscope (objective 50x). The laser power impinging on the cell window or on the dry sample was in the range from 1 to 5 mW. The spectrometer was calibrated by using the mode of Si at 520.2 cm^{-1}.

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