Specific Raman Signatures of a Dimetallofullerene Peapod

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We report on the Raman spectroscopy of a dimetallofullerene peapod, $(La_2@C_{80})_m$@SWNT. Drastic changes are observed with respect to pristine nanotubes. A sharp intense line at 142 cm^{-1} is interpreted as a signature of polymerization of the encapsulated metallofullerenes. Additional strong signatures appear at about 400, 520, and 640 cm^{-1}, respectively. Their intensity suggests the existence of an enhancement effect. The stiffening and the up-shift of the G-band modes appear to imply that a charge transfer process between the nanotube and the peas occurs.

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Recent experimental efforts in the field of nanotubes have resulted in the synthesis of a new class of hybrid materials, the so-called peapods. A peapod is a single-wall nanotube (SWNT), which encapsulates several fullerenes. In addition to the simplest peapod, $(C_{60})_m$@SWNT [1], more complex peapods have been obtained, where C_{60}'s are replaced by metallofullerenes (MFs) [2], which fill the SWNTs [3]. A new challenge in the future is likely to be the question of how one can control the electronic properties of peapods, not only by varying the inserted metallofullerene but also possibly by controlling the filling yield and the packing of the MFs inside the tube.

Detailed information on metallofullerene peapods has been derived from high resolution transmission electron microscopy and electron energy loss spectroscopy measurements, both for $(Gd@C_{82})_m$@SWNTs [3] and for $(La_2@C_{80})_m$@SWNTs [4]. In the latter case, the experimental results indicate that there must be a charge transfer between the cage and the tube. The change of conduction properties of SWNTs upon metallofullerene filling has been studied for $(Dy@C_{82})_m$@SWNTs [5]. A low-temperature scanning tunneling microscopy study has recently shown that a band gap modulation occurs in $(Gd@C_{82})_m$@SWNT peapods and also a possible deformation of the tubes [6]. This observation is important since it indicates the possibility of transforming a nanotube into a multiple quantum dot device. Several Raman spectroscopy studies of both fullerene and nonfullerene peapods have been reported [7–11] in the past two years. They have shown that, in addition to a modification of the intensity distribution of the lines of the pristine components, an additional Raman line due to dimerization of the encapsulated C_{60}'s in the $(C_{60})_m$@SWNT peapod may also occur. Theoretical treatment thus far has been restricted to the simple peapod, $(C_{60})_m$@SWNT [12,13].

In this Letter we report a Raman study of $(La_2@C_{80})_m$@SWNTs dimetallofullerene peapods. The synthesis procedure of $(La_2@C_{80})_m$@SWNTs is similar to that used to produce $(Gd@C_{82})_m$@SWNTs peapods [6]. Our Raman setup has been described previously [11,14]. Briefly, the setup is a confocal microscope used in a backscattering configuration. A high numerical objective, ×100, 1.3 NA, allows us to probe the sample with a high spatial resolution of the order of 400 nm. The signal is sent to a spectrometer equipped with a back-illuminated N_2-cooled charge-coupled device camera. The spectral resolution is 3 cm^{-1}. We used as excitation radiation the 514, 496, 488, and 476 nm Argon laser lines, varying the power between 0.1 and 10 mW. The Raman process is not resonant for nanotubes in this energy range. Surface-enhanced Raman scattering is not involved in the presented results. The diluted peapod sample has been stirred gently for about 30 to 60 min in ethanol prior to spin coating. Finally, we have used a Raman imaging process similar to that involved in the study of perylene-doped nanotubes, in order to determine the localization and analyze the different species present in the heterogeneous diluted samples [11]. It should be noted that different species coexist in our sample, namely, peapods, peas intercalated into nanotube bundles as well as pristine tubes.

Figure 1 shows typical low-frequency spectra observed at different locations. The top spectrum [Fig. 1(a)] shows a strong double-bump structure extending from 160 to 220 cm^{-1}. It corresponds to the radial breathing modes (RBMs) of pristine tubes and its structure is characteristic of the diameter distribution of the nanotubes. This distribution can be analyzed by using the well-established functional relation $d = \alpha/\omega$, where d is the tube diameter, ω is the frequency of the relevant RBM, and α is a constant, with a mean value of 234 cm^{-1} [10]. Based on this relation we find that the tube diameter distribution peaks at 1.25 nm while the contribution of pristine tubes of diameters larger than 1.4 nm is very low. In addition to this line a structured background is visible. This must be done by peas located outside tube bundles. Its shape, in fact, is similar to the signal that we have recently obtained for $La_2@C_{80}$'s alone [15]. The broad structures come from the many modes observed in the range 120–700 cm^{-1} that partly merge.

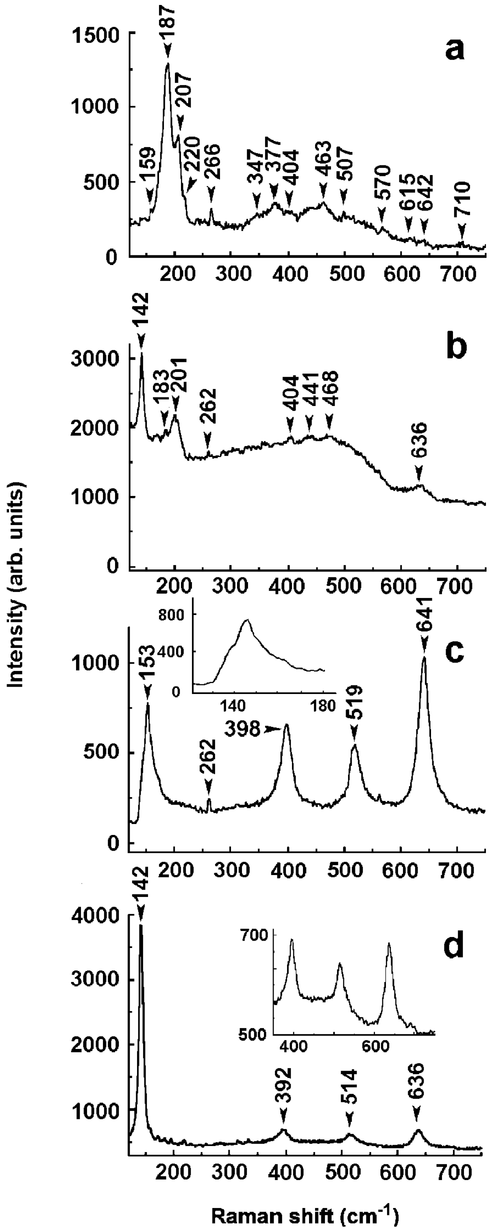

FIG. 1. Low-frequency Raman spectra of pristine tubes and of $(La_2@C_{80})_m$@SWNT peapods. (a) RBMs of pristine tubes; $\lambda = 514$ nm and $P = 10$ mW. (b) Raman signal of metallofullerenes intercalated between nanotubes. Width of the signal at 142 cm^{-1}: 7 cm^{-1}; $\lambda = 488$ nm and $P = 2.5$ mW. (c) Peapod Raman spectrum at low excitation energy; $\lambda = 488$ nm and $P = 0.1$ mW, respectively. Inset: magnification of the RBM signal at 153 cm^{-1} . (d) Typical peapod spectrum in the case of increased power; $\lambda = 514$ nm and $P = 1.5$ mW, respectively. Inset: magnification of the intermediate-range spectrum.

The RBM structure is still visible in Fig. 1(b) but an additional sharp line with a width of 7 cm^{-1} appears at 142 cm^{-1}. Both lines are superimposed on a background, which is smoother than in the previous spectrum, but which presents a similar overall shape. The line at 142 cm^{-1} is always observed at the same frequency when the excitation wavelength is changed, but it appears only when the power of the excitation exceeds 1 mW. These observations suggest that the line at 142 cm^{-1} might correspond to a Raman mode of $(La_2@C_{80})_2$ dimers or more generally of polymerized $(La_2@C_{80})_n$'s, which we photoinduced. This is in line with previous studies [16–19]. Because of the lowering of symmetry, additional modes appear that are located in the low-frequency region. We have observed several lines below 250 cm^{-1} also in the spectrum of diluted pristine $(La_2@C_{80})$'s, but never the line at 142 cm^{-1} [15]. This appears to imply that polymerization is favored when the peas are sufficiently close to each other or when they are constrained. In our diluted samples of peapods, this happens for peas that are localized between the tubes of bundles. Then these peas are partly protected against oxidation, and they can polymerize under irradiation. The numerous modes of $(La_2@C_{80})_n$'s merge to produce the large bump background in the intermediate-frequency range.

Figure 1(c) displays another type of typical spectrum. The double-bump structure in the RBM domain has disappeared and instead a single asymmetric line at 153 cm^{-1} dominates the spectrum. The intensity of this line is in a ratio of the order of 50:1 with respect to the pristine tube RBMs, for a similar excitation energy. This line is quite narrow, strong, and clearly outside the frequency range of pristine tube RBMs. The relevant G-band signal is moreover much weaker. These observations exclude the fact that this signal comes from pristine nanotubes. In addition, there are three strong lines at 397, 519, and 641 cm^{-1}, respectively. We interpret these results as follows. According to a synchrotron radiation powder diffraction study, the La-La and the La-cage distances in $La_2@C_{80}$ are 3.84 and 2.39 Å, respectively [20]. This means that the diameter of the metallofullerene must be about 8.62 Å. The van der Waals interaction potential between a spherical fullerene and a single-wall nanotube is minimized for a distance parameter equal to 3.354 Å, close to the distance between the graphene sheets in graphite [21]. Neglecting additional interactions, the estimated diameter of the relevant tube that can encapsulate $La_2@C_{80}$'s is then $8.6 + 2 \times 3.35 = 15.3$ Å. The relation $d = \alpha/\omega$ predicts the RBM frequency to be about 153 cm^{-1}. This value coincides with the measured frequency, suggesting that the peak at 153 cm^{-1} indeed corresponds to RBMs of peapods. The asymmetry of the line indicates that nanotubes of diameters close to 1.53 nm give a contribution to the signal also, but it is weaker [Fig. 1(c) inset]. The high intensity of the 153 cm^{-1} line remains to be explained. A possible enhancement of the signal of the relevant tubes relies on the possible existence of a nearly free electron state (NFE), because of the hollow space between the encapsulated MFs and the tube. NFE states have been predicted for nanotubes and nanotube bundles [12,22]. The presence of an NFE-like state could explain a diameter selective increase of the Raman process cross section since the probability that a NFE sate exists in peapods of smaller diameters is weaker. Let us now turn to the discussion of the three lines that appear in the intermediate-frequency range. Their intensity has the same order of magnitude as that of the RBM mode at 153 cm^{-1}. These three lines could be related to particular $\mathrm{La}_2@\mathrm{C}_{80}$ modes that are enhanced upon encapsulation. Surprisingly, no other specific strong signal appears in the studied frequency range, apart from the line at 153 cm^{-1}. This indicates either a selective enhancement of these particular modes or a large softening of the other modes, as is observed, for example, in the case of charge transfer between the alkali and the tubes in alkali-doped tubes [23,24]. An alternative explanation is that the three lines, or part of them, correspond to modes of nanotubes. Two processes could explain the emergence of modes of high intensity in this intermediate-frequency range. The first one is a process similar to that involved in finite-size tubes [25]. In peapods, the equivalent of the finite-size tubes should be the parts of the tube comprised between two neighbor metallofullerenes. But, the nonmonotonous decay of the peak intensities with increasing frequencies, conjugated with the absence of additional peaks in the lower frequency range, nearly precludes this possibility. An alternative process involving double resonance Raman scattering has been recently invoked [26]. As demonstrated by the observation of gap modulation in peapods [6], the MFs can be considered as local "defects" in peapods. As a result, the probability of diffusion of phonons is much increased and so is the probability for double resonance. This process activates modes, whose frequency depends on the phonon dispersion curves and on the electronic band structures. The frequency of the three lines does not depend on the excitation energy in the studied range. It implies that the relevant dispersion curves of the phonons are almost flat in the -vector range under consideration, assuming that the double resonance effect indeed contributes to these structures. Finally, when the excitation energy increases, we obtain the spectrum of Fig. 1(d) instead of that of Fig. 1(c). The sharp line at 142 cm^{-1} is recovered. Its high intensity prevents us from observing the peapod RBM at 153 cm^{-1}, even if the latter is present. The three other strong lines still appear with a slight downshift of 6 cm^{-1}. This signal does not change upon irradiation, even after a long time, contrary to what is often observed on pure metallofullerenes at room temperature. This spectrum can be interpreted as a signature of polymerization of the peas inside the nanotube, in agreement with the previous observation of dimerization in peapods [8].

Finally, we briefly discuss the signal recorded in the frequency domain of the G band of nanotubes. The overall shape of this band is the same for peapods [Figs. 2(b) and

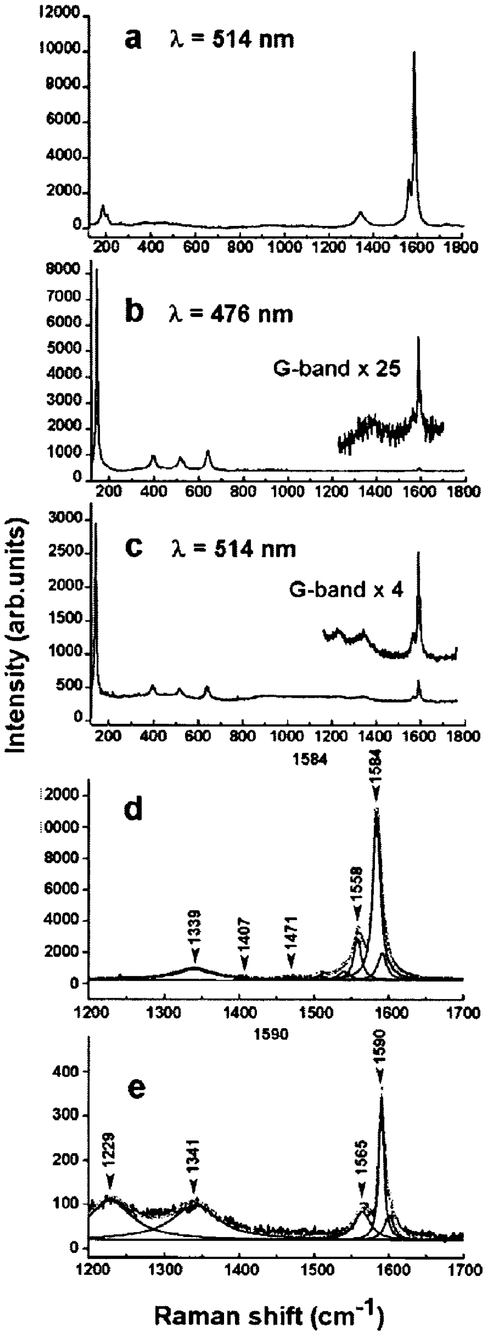

FIG. 2. Raman spectrum of pristine tubes and $(\mathrm{La}_2@\mathrm{C}_{80})_m$@SWNT peapods including the G band. (a) Spectrum of the pristine tubes [see relevant Fig. 1(a)]. (b) Signal of peapods: $\lambda = 476$ nm and $P = 1.4$ mW. (c) Signal of peapods at a different sample location: $\lambda = 514$ nm and $P = 1.5$ mW. A comparison between (b) and (c) demonstrates that the spectral features are similar in both cases. (d) Lorentzian-type fit of the G band corresponding to (a). The main lines of the G band peak at 1584 cm^{-1} (width 12 cm^{-1}) and at 1558 cm^{-1}. The broad D band is observed at 1339 cm^{-1}. Two additional lines at 1407 and 1471 cm^{-1} can be assigned to metallofullerenes. (e) Corresponding fit of the G band in the case (c) of peapods. The G-band lines are upshifted to 1590 cm^{-1} (width 7 cm^{-1}) and 1565 cm^{-1}.

2(c)] as for pristine tubes [Fig. 2(a)]. It shows the familiar double-bump structure in the 1500–1600 cm^{-1} range, but, whereas this band dominates the spectrum in pristine tubes, its highest recorded intensity is of the same order of magnitude as that of the intermediate range lines in peapods. Its intensity ratio is at most of the order of 1:8 with respect to the sharp line at 142 cm^{-1}. In addition, there is a systematic up-shift of the frequencies of the G-band modes of the order of 6 cm^{-1} from pristine tubes to peapods and the signal gets sharper. These observations can be compared to the results observed upon doping of the SWNTs with acceptors [27]. The charge transfer from the carbon tube atoms to the acceptor (Br_2 or I_2) results in mode stiffening and frequency up-shift. The characteristics of the peapod's G band strongly suggest that a charge transfer takes place from the SWNTs to the MFs. This conclusion is in agreement with the observation of a p-type semiconducting behavior at room temperature in $(\mathrm{Dy@C}_{82})_m\mathrm{@SWNTs}$ [5]. Besides additional arguments, the low intensity of the G band no doubt reflects the low number of peapods that are probed at a given location in the diluted sample. The drastic intensity difference between the line at 142 cm^{-1} and the G band is in line with a large enhancement of the four "low-frequency" modes. Additionally, the above-mentioned double resonance process or the presence of a NFE state can contribute to enhance the intensity of the intermediate-frequency signals, and at the same time to decrease the intensity of the tangential modes of the G band.

In summary, the Raman spectrum of the studied dimetallofullerene peapods differs from both the Raman spectrum of the SWNTs and that of the metallofullerenes alone. New lines are observed at the same frequency, whatever the excitation energy in the range 476–514 nm. The residual G band itself sharpens with respect to that of pristine tubes. The high intensity of the low- and the intermediate-frequency domain signatures shows that these Raman signals are strongly enhanced. Several effects, such as the presence of a NFE-like state or double resonance effects, may be invoked to explain their intensity. We hope that these results will stimulate theoretical work on metallofullerene peapods.

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