Two Positions of Potassium in Chemically Doped C_{60} Peapods: An in situ Spectroelectrochemical Study

Martin Kalbáč,[*,†,‡] **Ladislav Kavan,**[†] **Markéta Zukalová,**[†] **and Lothar Dunsch**[‡]

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague 8, Czech Republic, and Institute of Solid State and Materials Research, Helmholtztstr. 20, D - 01069 Dresden, Germany

The state of doping of fullerene peapods C_{60}@SWCNT treated with K vapor was studied by in situ Raman spectroelectrochemistry. For all samples under study, a heavy chemical n doping was proved by the vanishing of the radial breathing mode and the downshift of tangential displacement mode. The K-treated peapods remain partly doped even if they are exposed to humid air. The $A_g(2)$ mode of intratubular fullerene in K-doped peapods in contact with air was still redshifted as referred to its position in pristine peapods. Potassium inserted into the peapods is the reason for the air-insensitive residual doping, which can be removed only by electrochemical oxidation. This indicates the presence of two positions of potassium in doped sample.

1. Introduction

Fullerene peapods first observed by Smith et al.[1] are typical examples of a one-dimensional crystal inside single-wall carbon nanotubes (SWCNT). Recently, these advanced nanostructured materials were studied theoretically[2,3] and experimentally due to their unique electronic properties[4,5] and potential practical application, e.g., in high-temperature superconductors,[6] memory elements,[7] or nanoreactors.[8]

Raman spectroscopy of both SWCNT and fullerenes is resonant via the allowed optical transitions in these carbon nanostructures. Raman spectra of the fullerene peapods are determined by the superposition of vibrational features of both components. SWCNT are represented by radial breathing mode (RBM) at ca. $100-300$ cm^{-1} and tangential displacement mode (TG) at ca. $1500-1600$ cm^{-1}, which dominate the spectra. Less intense fullerene bands are observed at 270 cm^{-1}, $H_g(1)$; 430 cm^{-1}, $H_g(2)$; 494 cm^{-1}, $A_g(1)$; 709 cm^{-1}, $H_g(3)$; 769 cm^{-1}, $H_g(4)$; 1424 cm^{-1}, $H_g(7)$; and 1465 cm^{-1}, $A_g(2)$.

There are several studies on chemical[8,9] and electrochemical doping of fullerene peapods.[10] Chemical n and p doping of peapods was carried out by vapor of potassium and $FeCl_3$, respectively.[8] Both n and p doping of SWCNT shift the Fermi level energy, which leads to a bleaching of optical transitions between Van Hove singularities. Hence, the intensity of resonance Raman spectra of SWCNT decreases during the n/p doping. The frequencies of C_{60} fullerene were found to be unchanged after oxidative and low-level reductive doping with $FeCl_3$ and K, respectively.[8] This indicates that the charge transfer influences solely the SWCNT wall, but the C_{60} fullerene remains intact at these conditions. Heavily K-doped samples exhibit a decrease of the C_{60} band intensities and their frequency shifts, which are reminiscent of those in fullerides.[8] Heavy n doping indicated, reportedly, intratubular C_{60}^{6-} [8,9] followed by the formation of one-dimensional metallic polymer of single-bonded

fullerides. The polymer is characterized by two extra bands at 370 and 620 cm^{-1}.[9]

Electrochemical doping of peapods is favored because of precise and easy control of the doping level.[10] Nonaqueous electrolyte solutions have a sufficient potential window from ca. -1.5 to $+1.5$ V vs an Ag/AgCl reference electrode. Similar to chemical doping, bleaching of the Raman modes of SWCNT and shifts of the TG mode are observed. In the case of anodic doping, also significant enhancement of the intensities was reported for the C_{60} fullerene modes in peapods.[11] However, the characteristic softening of the $A_g(2)$ mode, which would indicate the intratubular fulleride, was not detectable during electrochemical doping. Furthermore, no bands corresponding to a C_{60} polymer were observed in cathodically n-doped peapods,[11] and we may note that the polymer bands seem to be missing also in some samples of K-doped peapods.[8] Both chemical and electrochemical doping are powerful tools for the variation of the electronic properties of carbon nanostructures. To the best of our knowledge, this is a first attempt to combine both methods for exploring of the doping state of C_{60}@SWCNT in detail and for clarifying the differences between chemical and electrochemical doping.

2. Experimental Section

The sample of C_{60}@SWCNT peapods (filling ratio 85%) was available from our previous work.[11] The sample was outgassed at 285 °C/10^{-5} Pa (the residual gas was He) and subsequently exposed at 177 °C to potassium vapor for $25-40$ h. The reaction took place in an all-glass ampule interconnected to a Raman optical cell with Pyrex glass window. (Note: a quartz window cannot be used at these experimental conditions as it reacts with K vapor.) The rest of the K was finally distilled off at 200 °C/10^{-5} Pa with cooling of the opposite end of the ampule. These samples are denoted as A. A part of A was exposed to the atmosphere of nitrogen-filled glovebox (M. Braun, <1 ppm O_2, <1 ppm H_2O) and stored under nitrogen, and its Raman spectrum was measured in a N_2-filled optical cell (samples B). The third part of sample A was treated in air or in air saturated with water vapor at 90 °C (samples C).

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 * To whom correspondence may be addressed. E-mail: kalbac@jh-inst.cas.cz.

 † Academy of Sciences of the Czech Republic.
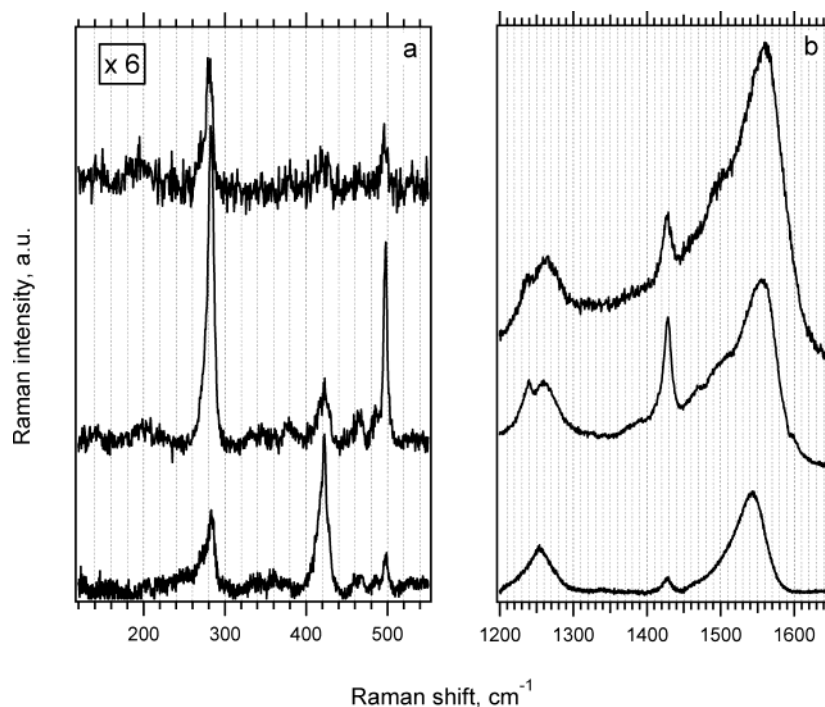
 ‡ Institute of Solid State and Materials Research.

Figure 1. Raman response of the (a) RBM and (b) TG modes of C_{60} peapods chemically doped with potassium. The spectra were measured on a dry sample in the form of buckypaper. Intensities of spectra were normalized using the F_{1g} line of Si at 520.2 cm^{-1}. The excitation wavelengths were, from top to bottom, 2.54, 2.41, and 1.91 eV. Spectra were offset for clarity.

A thin-film electrode was prepared by evaporation of the sonicated (approximately 15 min.) ethanolic slurry of the sample C on Pt electrode in air. The film electrode was outgassed overnight at 90 °C in a vacuum (10^{-1} Pa) and then mounted in a spectroelectrochemical cell in a glovebox. The cell was equipped with a Pt-counter and Ag-wire pseudoreference electrode. LiClO$_4$ (0.2 M) in dry acetonitrile was used as the supporting electrolyte. Electrochemical experiments were carried out using PG 300 (HEKA) or EG&G PAR 273A potentiostats.

The Raman spectra were measured on a T-64000 spectrometer (Instruments, SA) interfaced to an Olympus BH2 microscope (the laser power impinging on the sample or cell window was between 1 and 5 mW). Spectra were excited by a Kr$^+$ laser at 1.91 eV or Ar$^+$ laser at 2.41 and 2.54 eV (Innova 305, Coherent).

The Raman spectrometer was calibrated before each set of measurements by using the F_{1g} line of Si at 520.2 cm^{-1}. The spot size was ca. 0.1 mm × 0.1 mm.

3. Results and Discussion

The optimum diameter of the nanotube, which could encase the C_{60} molecule is 1.39 nm;[3] the maximum tube diameter is, in principle, not limited. However, the accommodation of fullerene is energetically less favored with increasing tube radius.[2] Our peapod sample has narrow diameter distribution, and it is close to the ideal value of 1.4 nm.[10,11] Calculations of electronic structure[12] show that photons of 1.91 eV resonate with transition ν_m^1/c_m^1 in metallic SWCNT, and photons of 2.41 and 2.54 eV resonate with transition ν_s^3/c_s^3 in semiconducting SWCNT. Figure 1 displays the spectra of the K-doped C_{60}@SWCNT peapod (sample A) measured with three different excitation energies. The overall intensity of our spectra is lower compared to undoped sample (not shown). Furthermore, the band of RBM vanished almost completely, which indicates a complete filling of the c_s^3 states in SWCNT by our method of chemical doping.

The bands of intratubular fullerene dominate the low-frequency region and, in agreement with previous results for K-doped samples,[8] are shifted as compared to those of the pristine peapod. The $H_g(1)$ and $A_g(1)$ modes were hardened to 282 and 498 cm^{-1}, respectively, and the $H_g(2)$ mode was softened to 423 cm^{-1}. The Fano broadening of the $H_g(1)$ mode due to the metallic state of doped fullerene was also confirmed in our heavily doped sample. The positions of lines are independent of the excitation energies, but the relative intensities are different.

The $A_g(2)$ mode of fullerene is known to be redshifted linearly with the number of electrons per cage in n-doped materials. The softening is about 6.5 cm^{-1} per one extra electron transferred to the cage.[13] The $A_g(2)$ mode of our heavily doped peapod is at 1428 cm^{-1}, which corresponds to ca. 6 extra electrons in C_{60}. This is in accord with previous studies.[8,9] The downshift is slightly higher than expected for C_{60}^{6-}, which was explained by the formation of a polymer.[8,9] However, it could be alternatively caused by the influence of a surrounding tube or one-dimensional assembly of fullerene. The polymer-related bands at 370 and 620 cm^{-1} are not detectable either (Figure 1).

The intensity of the TG mode is also very low compared to that in pristine samples (Figure 1). In contrast to other work,[8] we observed a downshift of the TG mode frequency. The downshift of TG was also observed for heavily doped SWCNT.[14-16] In this case, the downshift was explained by a "phase" transformation of crystalline SWCNT ropes.[16] A more detailed analysis of SWCNT doping has shown that in the first stage of doping the TG mode is slightly upshifted due to a dominant contribution of structural effects (structural disorder, hardening of the lattice via interactions between the tube and the alkali metal, etc.). After further doping, the downshift due to the "phase" transformation starts to dominate.[16] Similar effects are expected for peapods, because the intratubular fullerene would not affect the assembling of the tubes into bundles. Hence, the samples are heavily doped and the spectrum of the new
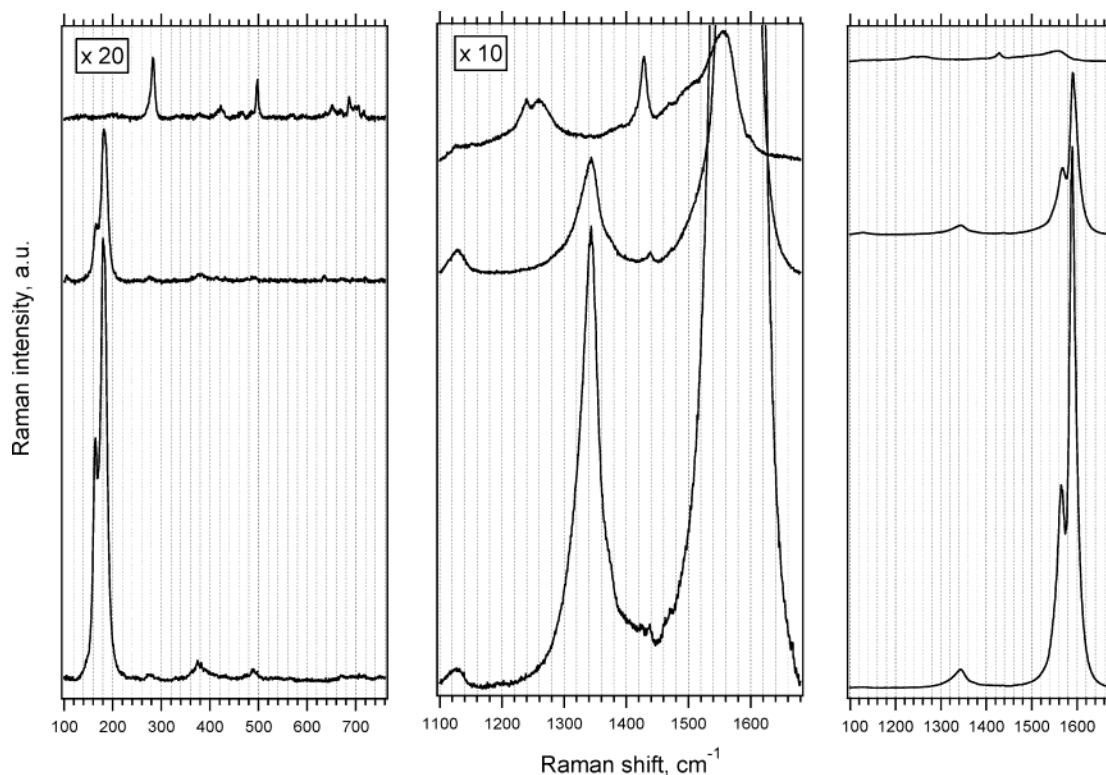
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Figure 2. Raman response of C$_{60}$ peapods doped with potassium. From top to bottom: sample A (as received and handled only in a vacuum); sample B (after exposure to nitrogen atmosphere); and sample C (after handling in humid air, see the Experimental Section). The spectra were measured on dry buckypaper. Intensities of spectra were normalized using the F$_{1g}$ line of Si at 520.2 cm^{-1}. The excitation wavelength was 2.41 eV. Spectra were offset for clarity.

crystalline phase was observed. The authors of previous works[8,9] did not achieve as high doping as is presented in this work, since they observed only a small upshift of the TG mode, which corresponds to the first stage of doping. The high level of doping of our samples is also confirmed by the vanishing of the RBM band (see above). The TG peaks were at 1543, 1556, and 1561 cm^{-1} for the excitation photons 1.91, 2.41, and 2.54 eV, respectively. This is consistent with the previously reported data for SWCNT.[14−16]

The spectra of samples A, B, and C excited by the green laser demonstrate that the intensity of SWCNT-related bands decreases in the series C > B > A, as expected for the increase of doping level in the same order. The RBM bands are found between 165 and 185 cm^{-1} for both samples B and C. If we neglect the intertube interactions in a bundle, the tube diameter (*d*) is known to scale inversely with the RBM frequency (*ω*)

$$d \approx a/\omega$$

where the constant (*a*) was reported to be in the range from 224 to 248 nm/cm^{-1}.[3,9,17] The calculated tube diameters for the samples B and C are between 1.2 and 1.5 nm, which corresponds to the diameters of pristine peapods. This is also consistent with other results.[8] The bands of the TG mode of samples B and C are blueshifted approaching their original position in the pristine peapod (1592 cm^{-1}). It confirms the partial reversion of the peapods to the original charge state. The recovery of the original Raman spectrum of the nanotubes confirms that the nanotubes are not destroyed during the potassium doping even if the sample is heavily doped.

The relative intensities of the fullerene bands decrease in the series A > B ≈ C (Figure 2), i.e., in the series of decreasing doping level. This contrasts with the previous Raman studies at 20 K, where the opposite tendency was reported, i.e., the

bands of intratubular fullerene quenched after the progressive treatment with K vapor.[8] This difference could be explained by the higher doping level of our samples compared to those in the previous work.[8] However, the original position of the fullerene bands in pristine peapods is only partly recovered if the sample is exposed to air. The A$_g$(2) band is shifted to 1440 cm^{-1} in both samples B and C, which indicates that the fullerene remains partly doped (by ca. 4 extra electrons per cage) upon exposure to air. Furthermore, the intensities of nanotube modes were smaller than those of pristine peapods, which also confirms the residual doping. A similar conclusion follows from the measurements with the excitation energies of 2.41 and 1.91 eV (data not shown).

Apparently, the chemically K-doped peapods are very sensitive in the first stage of handling to traces of oxygen and humidity. This is demonstrated even upon exposure to nitrogen atmosphere containing <1 ppm O$_2$ and H$_2$O (sample B). The K doping is not fully removed even if the samples are in contact with humid air at 90 °C (sample C). The rapidly extractible part of potassium occupies obviously the positions between the SWCNTs in bundles. However, Farajian et al.[18] predicted a potassium insertion into the nanotube through the wall. Recently, it was confirmed that potassium can penetrate into open SWCNTs.[19] As the peapods consist of opened tubes, the insertion of potassium into the peapods has to be taken in account. If we accept the possibility of intratube potassium, we may explain the high stability of residual doping. Therefore we propose that potassium also penetrates the interior of peapods by doping. Exposition to oxygen and humidity deactivates the potassium doping outside the peapods, but it does not affect the potassium fixed inside the peapod as well as the charged fullerene state. A high stability of the residual doping is observed. Our data are also in a qualitative accord with the
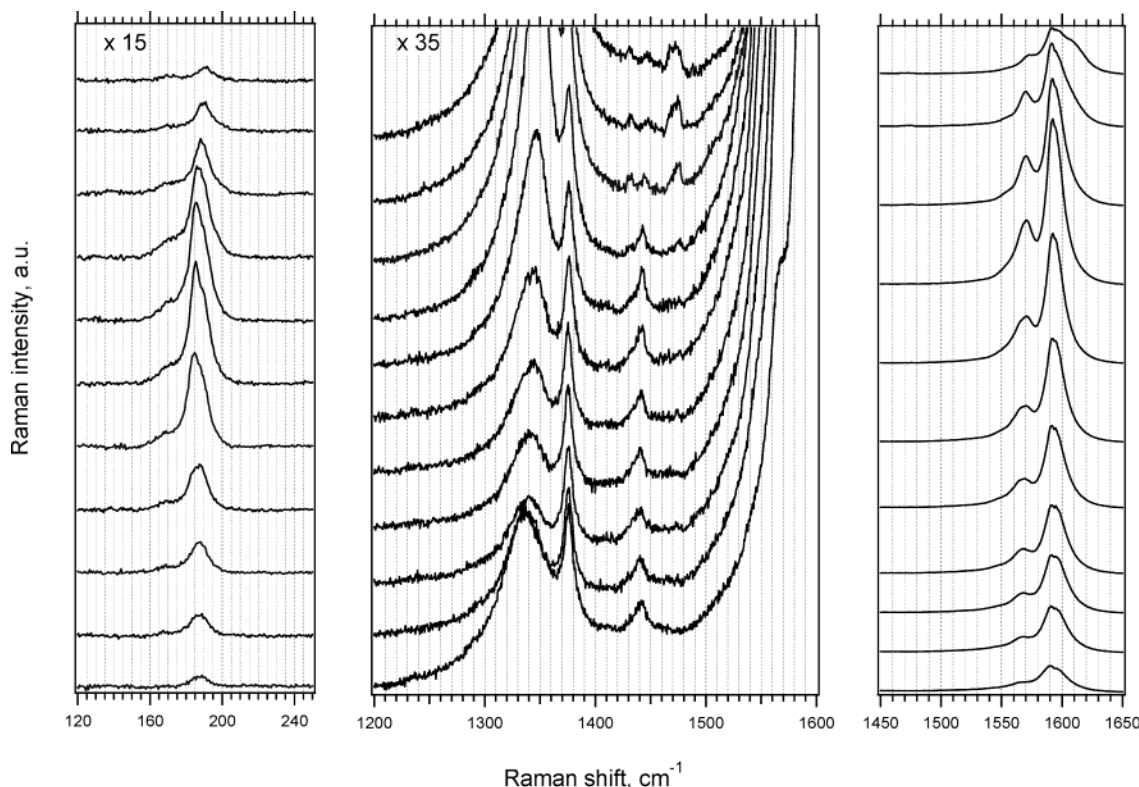
Figure 3. Raman response of K-doped C_{60}@SWCNT (sample C after handling in air) at different electrode potentials varied by 0.3 V from 1.5 to −1.5 V vs Ag pseudoreference electrode (curves from top to bottom). Spectra were excited at 2.41 eV. Curves are offset for clarity, but the intensity scale is identical for all spectra in the respective window. The peak at 1374.5 cm^{-1} belongs to acetonitrile.

results of Iijima et al.,[20] demonstrating a very high stability of intratubular C_{60} against oxygen.

To get further insight into the doping of peapods, the chemically K-doped sample (C) was subjected to electrochemical treatment (Figure 3). The Raman spectra of peapods were measured at different electrode potentials from −1.5 to 1.5 V. To avoid uncontrolled changes of the doping state, the measurement was started at 0 V vs Ag/Ag^+, which is close to the open-circuit potential of a freshly assembled spectroelectrochemical cell. Subsequently, the potential was moved to −1.5 V and then to +1.5 V vs Ag/Ag^+. Cathodic charging, which is equivalent to weak potassium doping, decreases the intensity of nanotube-related bands. This resembles the electrochemical doping of the pristine sample.[10] The bleaching of higher-frequency RBM bands (180−190 cm^{-1}) is smaller than that of lower-frequency RBM bands (165−175 cm^{-1}), which matches the previous data on pristine peapods[11] and nanotubes.[21] The final RBM intensity at −1.5 V is approximately 10% of the original intensity at 0 V. The tangential mode exhibits a decrease to approximately 20% of its original intensity. This is also in good agreement with our previous data on pristine C_{60}@SWCNT.[10] No significant shift of the TG mode was observed upon cathodic charging of K-doped peapod. This differs from the behavior of pristine peapod samples, where a small shift was found.[11] The shift of the TG mode is connected with the softening or hardening of the graphene sheet. We assume that intratubular potassium ions attenuate the effect of the electrochemical charging. As the shift of TG mode is very small even during cathodic charging of potassium-free peapod,[11] the influence of intratubular potassium ions could reduce it below the detectable level.

The intensity of low-frequency fullerene modes was very weak; hence, we shall further concentrate on the $A_g(2)$ mode, which is reasonably resolved around 1440 cm^{-1}. The position of this band remains unchanged during the cathodic charging

of the K-doped peapods. It is only slightly decreased in intensity. This contrasts with the behavior of pristine peapods, where the $A_g(2)$ mode rapidly bleaches below the detectable intensity at cathodic potentials.[11] However, it is qualitatively consistent with our hypothesis of co-inserted potassium in heavily K-doped peapods. The intratubular fulleride of the assumed composition of K_4C_{60} (see bellow) remains intact even upon air exposure and handling of the sample in air before the spectroelectrochemical tests. Subsequent cathodic charging does not markedly modify the state of the intratubular species; hence, we can exclude that additional electrons and compensating counterions penetrate into the peapod. This could be easily understood: the C_{60}^{4-} is electrochemically generated at −2.35 V vs Fc/Fc^+ (Fc = ferrocene),[22] which is considerably more negative compared to the lowest potential applied in this study (−1.5 V vs Ag/Ag^+). Therefore, no additional reduction and no shift of the $A_g(2)$ mode is observed during cathodic scan. A small decrease of the $A_g(2)$ intensity could be explained by shadowing of the fullerene with higher electron density on the peapod wall. The qualitatively different behavior of K-free and K-doped peapods can also be discussed in terms of electronic structure of these two materials. The position of the fullerene LUMO in a K-free peapod is within the band gap and near the Fermi level of SWCNT.[11] Therefore electrons can be readily transferred from the SWCNT wall to the LUMO of fullerene during the cathodic charging. This efficiently quenches the HOMO−LUMO transition and the corresponding resonance Raman scattering. On the other hand, the intratubular K−fulleride is markedly less sensitive to electrochemical perturbations on the wall, as the LUMO of fulleride has larger separation from the Fermi level of SWCNT.

The anodic charging causes the overall bleaching of RBM and TG bands as in the case of pristine peapods.[11] However, the fine structure of TG shows a more complex feedback to

anodic potentials as compared to the TG band of pristine peapods. Whereas the pristine peapods exhibit just a monotonic blueshift of the TG peak upon anodic charging, the K-doped peapod exhibits a splitting of the TG mode into blueshifted and potential-independent components (Figure 3, upper curves on the right panel). To explain such a different behavior, we assume that holes introduced by anodic doping are quenched by the intratubular fulleride and therefore the TG mode is not upshifted. The appearance of a blueshifted component (1608 cm^{-1} at 1.5 V) is consistent with an identical behavior of pristine peapods at anodic charging.[11] We interpret this effect as a result of the presence of some K-undoped C$_{60}$ in real peapod materials (sample C). We may assume that K atoms penetrate preferentially via defects in the SWCNT wall. (This idea is reminiscent of a model suggested by Tomanek, that even the synthesis of peapods is controlled by the penetration of C$_{60}$ through defect wall rather than the decapped ends of the SWCNT precursor.)[23] Hence, there may persist extended defect-free areas in the real peapod, which are nonpermeable for K atoms. These areas contain uncharged C$_{60}$ peapods, which mimic the behavior of pristine peapod. Also the behavior of the A$_g$(2) mode is consistent with the hypothesis of the bimodal (C$_{60}$ and C$_{60}^{x-}$) configuration of K-doped peapods, vide infra.

A spot "burning" has been frequently observed after prolonged laser irradiation of anodically ($E > 1.2$ V vs Ag/Ag$^+$) charged SWCNT and peapods.[10,11,21] As previously reported, no destruction occurred outside the spot nor on the spot if the sample was less anodically charged.[10,11] Furthermore a higher intensity of both the RBM and TG modes was found if we repeat the measurement at the "burned spot" at zero potential compared to the starting spectra of this sample at 0 V vs Ag/Ag$^+$. The spot burning seems to be triggered by a particular larger destruction of the SWCNT wall, which allows the electrolyte to penetrate inside the peapod. This deactivates the inserted potassium and leads to the increase of SWCNT bands intensity.

The behavior of the pentagonal pinch mode A$_g$(2) is very interesting. This band appears at 1465 cm^{-1} with a satellite line at 1474 cm^{-1} in pristine peapods.[11] K doping shifts its position to 1428 cm^{-1} (samples A and B), which is consistent with the reports of other authors,[8,9] indicating the presence of intratubular C$_{60}^{6-}$. This deeply reduced fullerene might still survive even in samples C as the A$_g$(2) band is quite broad (Figure 3), but the peak at 1440 cm^{-1} is assignable to C$_{60}^{4-}$. The peak at 1440 cm^{-1} ($\sim$C$_{60}^{4-}$) persists at all potentials between -1.5 to 1.5 V vs Ag/Ag$^+$; albeit we observe the usual charge-driven bleaching. However, at 0.6 V, the band at 1470 cm^{-1} starts to appear, close to the position of the A$_g$(2) mode in pristine peapods. This band is known to increase significantly in intensity without any frequency shift upon anodic charging.[11] The "anodic Raman enhancement", first observed in K-free C$_{60}$@SWCNT,[10,11] is reproduced here also in K-doped peapods (Figure 3). This confirms our hypothesis of undoped island at defect-free sites, where the K-atoms cannot penetrate into the peapod, vide ultra. The maximum intensity of the A$_g$(2) mode in the anodically charged K-doped sample is about one-third of the intensity of the anodically charged pristine peapod (if we normalize the intensities against the D band). Hence, we can estimate that approximately $^1/_3$ of the fullerene molecules were not reached by potassium. At potentials >0.9 V, a new band develops at around 1430 cm^{-1}. The same effect was observed also in pristine peapods, where this band was assigned to the "anodically enhanced" H$_g$(7) mode of C$_{60}$.[11] It is tempting to suggest the same interpretation also here, despite the fact that the relative intensity of this band is somewhat too large. Alternative assignment of the A$_g$(2) band at 1430 cm^{-1} to a deeply reduced fullerene ($\sim$C$_{60}^{6-}$) does not seem to be plausible at the conditions of strong anodic charging.

The doping process of chemically doped peapods is reasonably reversible. Only the intensity of the fullerene/fulleride bands tends to decrease during Raman measurements. We assume that this is due to oxidative spot burning. The defects in the tube wall allow the electrolyte to thrust in inner space and to oxidize irreversibly the fulleride. This is confirmed by the slight intensity enhancement of the tube-related modes.

4. Conclusion

The high level of chemical doping of C$_{60}$@SWCNT by potassium was demonstrated by the vanishing of the tube-related RBM band, by the downshift the TG mode, and by the slight overall increase of fullerene vibrational features. Despite exposing the K-doped peapods to air saturated with water vapor at 90 °C, the tube/fullerene bands did not recover their original positions and shapes. Therefore we assume that doping of peapods with potassium leads to an insertion of the alkali metal not only between the tubes in a bundle but also into the interior of the peapod. Thus the material formed has a characteristic spectral feature including the shift of A$_g$(2) and reduced intensity of RBM and TG mode of the outer SWCNT. The intratubular doping is also confirmed by the developing of the fullerene A$_g$(2) band during subsequent electrochemical charging of the chemically K-doped sample. This mode remains almost unchanged if we charge the K-doped peapods cathodically, but it is bleached when the sample is doped anodically. Therefore chemical and electrochemical doping are rather complementary than competitive processes. In other words, the heavy chemical doping leads to the insertion of potassium into the tube, which seems to be responsible for a downshift of the A$_g$(2) mode, whereas electrochemical doping introduces charges to fullerene only indirectly through the nanotube wall.

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