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Doping of C_{60} Fullerene Peapods with Lithium Vapor: Raman Spectroscopic and Spectroelectrochemical Studies

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Abstract: Raman spectroscopy and in situ Raman spectroelectrochemistry have been applied to the study of the lithium vapor doping of C_{60}@SWCNTs (peapods; SWCNT = single-walled carbon nanotube). A strong degree of doping was proven by the disappearance of the radial breathing mode (RBM) of the SWCNTs and by the attenuation of the tangential (TG) band intensity by two orders of magnitude. The lithium doping causes a downshift of the $A_g(2)$ mode of the intratubular C_{60} by 27 cm^{-1} and changes the resonance condition of the encapsulated fullerene. In contrast to potassium vapor doping, the strong downshift of the TG band was not observed for lithium doping. The peapods treated with lithium vapor remained partially doped even when they were exposed to humid air. This was reflected by a reduction in the intensity of the nanotube and the fullerene modes and by the change in the shape of the RBM band compared with that of the undoped sample. The $A_g(2)$ mode of the intratubular fullerene was not resolved after contact of the lithium-doped sample with water. Lithium insertion into the interior of a peapod and its strong interaction with the intratubular fullerene is suggested to be responsible for the air-insensitive residual doping. This residual doping was confirmed by in situ spectroelectrochemical measurements. The TG band of the lithium-doped peapods did not undergo an upshift during the anodic doping, which points to the formation of a stable exohedral metallofullerene peapod.

Keywords: electrochemistry · fullerenes · lithium · Raman spectroscopy · spectroelectrochemistry

Introduction

The tuning of the electronic structure of carbon nanostructures, such as single-walled carbon nanotubes (SWCNTs) and fullerene peapods (C_{60}@SWCNTs), is important for most applications of these materials in nanoelectronics. It has been shown that doping significantly influences the electronic properties of these materials.[1,2] The doping can be performed electrochemically or chemically. The electrochemical doping of peapods is in general preferred because it allows precise and easy control of the doping level.[1,3] Nonaqueous electrolyte solutions have a sufficiently large potential window, from around −1.5 to +1.5 V (vs. Ag/AgCl), for most doping reactions. However, electrochemically and chemically doped carbon nanostructures do not show the same properties.[2,4] For example, the characteristic softening of the C_{60}-related $A_g(2)$ mode induced by chemical n-doping was not detectable during electrochemical charging of C_{60} peapods at cathodic potentials.[2,4] We demonstrated previously that electrochemical and chemical doping of C_{60}@SWCNTs are governed by different mechanisms.[2] Electrochemical doping leads to charging of the wall of the SWCNTs, which slightly affects the intratubular fullerene. On the other hand, chemical doping with gaseous potassium influences both the SWCNTs and the intratubular C_{60} molecules[2,5] because the potassium vapor penetrates the tube to form an exohedral metallofullerene peapod.[2,5] This effect was confirmed by Iijima and co-workers by direct TEM observation.[6] Recently, Shinohara and co-workers[7] showed that an exohedral metallofullerene peapod can be formed directly from fulleride without any further doping. The exohedral metallofullerenes in peapods possess an exceptional stability because they are protected by the nanotube wall.[2,7] Even treatment of the samples with water did not complete-

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ly remove the alkali-metal ions from the potassium-doped peapods.[2] Exohedral metallofullerene peapods have been shown to be novel fullerene-based conductors with a reduced dimensionality compared with fullerene films.[8]

The exohedral metallofullerenes in peapods were formed by reactions with potassium[2,5,6,9] and cesium.[7] However, to the best of our knowledge, there is no comparable study of the doping of peapods by lithium. Among the reasons for this might be the technical difficulties associated with the use of lithium vapor in an ordinary glass vacuum apparatus. Nevertheless, lithium is of particular interest in this field due to its small atomic radius, which promotes its easy penetration into peapods and other carbonaceous nanostructures as well as graphite. This effect finds important applications in lithium-ion batteries. The special properties of lithium–carbon bonds are also a strong motivation for studies on lithium doping.[10]

Herein we present a Raman spectroscopic study of lithium-doped C_{60}@SWCNTs. C_{60}@SWCNTs serve as a convenient model to study the position of a compensating counterion in n-doped carbon nanostructures because the C_{60} molecule can be used as a marker.[2] The stability of the doped states can be tested by water treatment and by subsequent in situ Raman spectroelectrochemistry to follow changes in the electronic structure upon electrochemical charge transfer.

Results and discussion

Lithium doping: The SWCNT-related Raman features: The Raman spectra of peapods (Figure 1) excited by 2.54, 2.41, and 2.18 eV laser radiation show features characteristic of SWCNTs: the radial breathing mode (RBM) between 160 and 190 cm^{-1} and the tangential (TG) band at around 1595 cm^{-1}. The Raman features of the intratubular C_{60} fullerene are rather weak, hence only the most intense one, namely, the $A_g(2)$ mode, is shown. The Raman spectra of peapods (Figure 2) doped by lithium vapor and excited by the 2.54, 2.41, and 2.18 eV laser lines demonstrate that the overall spectral intensity of the doped sample is considerably smaller than that of the pristine sample (Figure 1). The band of the RBM has almost disappeared, which proves the high level of doping.

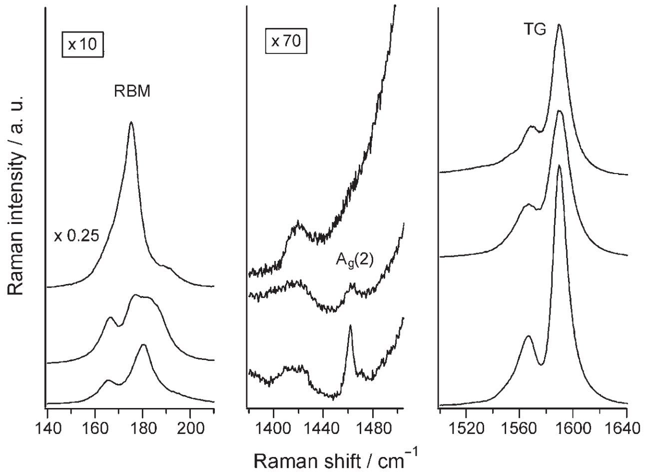

Figure 1. Raman spectra of pristine C_{60}@SWCNTs (excited at 2.18, 2.41, and 2.54 eV, from top to bottom). The intensities of the spectra were normalized by using the F_{1g} line of silicon at 520.2 cm^{-1}. The spectra are offset for clarity, but the intensity scale is identical for all the spectra in their respective windows (unless stated otherwise).

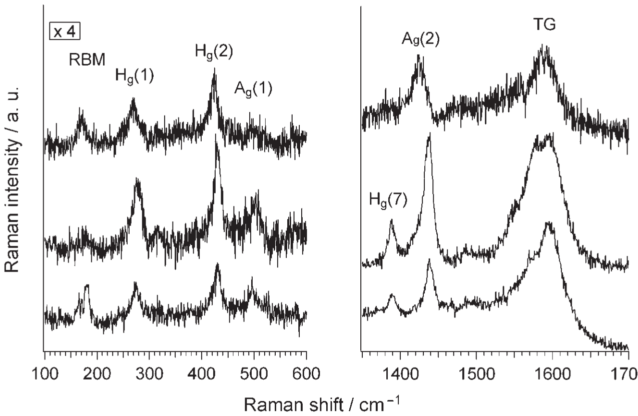

Figure 2. Raman spectra of lithium-doped C_{60}@SWCNTs (excited at 2.18, 2.41, and 2.54 eV, from top to bottom). The intensities of the spectra were normalized by using the F_{1g} line of silicon at 520.2 cm^{-1}. The spectra are offset for clarity, but the intensity scale is identical for all the spectra in their respective windows.

The intensity of the TG band of the lithium-doped sample is also very low compared with that in pristine samples (Figure 1). The decrease in the intensity of the TG band upon doping is about two orders of magnitude for all laser excitation energies. The dramatic change in the intensity of the Raman lines is explained by the doping-induced filling of the Van Hove singularities.[11,12] (The optical transitions between the particular singularities are blocked by doping. Because the optical transitions play a crucial role in the resonance enhancement of Raman spectra, the filling of the Van Hove singularities causes a suppression of the Raman signal.)

The behavior of the TG band frequency of doped nanotubes is still under debate, especially for n-doping.[1] For SWCNTs both frequency up- and downshifts have been reported depending on the level of doping and the type of counterion used (Li^+, K^+, Rb^+, Cs^+).[13–21] The detailed study by Chen at al.[20] showed that there are at least four stages in the doping procedure: 1) a long induction period, 2) a short interval in which the RBM and the TG band are bleached, 3) a slight upshift of the TG band, and 4) a strong downshift of the TG band up to saturation. The upshift of the TG band in the third stage of doping is consistent with a decrease in the C–C bond length within the tube wall. On the other hand, the strong softening of the TG band observed in the fourth stage of doping was previously attributed to a change in the tube–tube interaction.[22] Hence softening of the TG band was not expected for doped isolated SWCNTs. However, this is in contrast to experimental results that showed similar behavior of the TG band for isolated nanotubes.[19] Consequently, other effects like structural disorder, hardening of the lattice by interactions of the tube and the alkali-metal ion, and doping-induced renormalization of the phonon energy[23] must be considered. Similar effects were found for potassium-doped peapods because the intratubular fullerene does not affect the assembly of tubes into bundles.[2,4]

Owing to its small atomic radius, lithium is known to have unique properties among the alkali metals. Hence lithium doping is expected to give the doped material properties that are different from those of material doped with other alkali metals. Indeed, as shown in Figure 2, the TG mode frequency is much less sensitive to lithium doping than to potassium doping studied earlier.[2] Hence, lithium doping does not lead to the same effects.

Bands arising from the fullerene in undoped pristine peapods are observed at 270 ($H_g(1)$), 430 ($H_g(2)$), 494 ($A_g(1)$), 709 ($H_g(3)$), 769 ($H_g(4)$), 1424 ($H_g(7)$), and 1465 cm^{-1} ($A_g(2)$) for 2.54 eV laser radiation (not shown). Bands arising from the intratubular fullerene dominate the low-frequency region of lithium-doped peapods as the RBM of the tube disappears. Lithium vapor doping induces a change in the position of most of these bands. The $H_g(1)$ and $A_g(1)$ slightly harden to 275 and 496 cm^{-1}, respectively. On the other hand, the $H_g(7)$ and $A_g(2)$ bands soften to 1390 and 1437 cm^{-1}, respectively. The frequency of the $A_g(2)$ mode is known to be linearly redshifted with a number of extra electrons transferred to the fullerene. In the case of potassium vapor doping this redshift was about 6.5 cm^{-1} per electron.[24] For heavily doped samples the charge transfer is equivalent to six electrons on the C_{60} cage. As shown previously, such strong doping could be realized only by the penetration of potassium atoms into the peapod.[2,5] On the other hand, the $A_g(2)$ mode of the lithium-doped peapod is at 1437 cm^{-1}, which corresponds to about four extra electrons on C_{60} assuming the same relationship as that for potassium doping.

Strictly speaking, our assumption of an identical relationship for the redshift of the $A_g(2)$ band in lithium- and potassium-doped fullerene is not supported, but we note that the $A_g(2)$ mode of fulleride Li_4C_{60} exhibits a similar downshift[25,26] to that found for lithium-doped peapods in this work. Nevertheless, according to X-ray diffraction data the fulleride Li_4C_{60} forms a polymer with a two-dimensional architecture.[27] In this polymer the fullerenes are bonded by single C−C bonds and by "double" bonds that arise from a [2+2] cycloaddition reaction.[27] The formation of new polymeric bonds is believed to contribute to the downshift of the $A_g(2)$ mode of the fulleride Li_4C_{60} polymer. According to Wagberg et al.[25] the $A_g(2)$ mode is downshifted by 2.5 cm^{-1} per single bond and by 5.5 cm^{-1} per "double" bond. The total downshift is a sum of the downshift caused by charge transfer and by the formation of the polymer. According to this the charge transferred from lithium to C_{60} in the Li_4C_{60} case should be $[1469-(2\times5.5+2\times2.5)-1442]/6\approx2e$ (see ref. [26]), which corresponds formally to the transfer of 0.5 electrons per lithium atom. In the case of peapods, the formation of a two-dimensional polymer is clearly not possible for steric reasons. Indeed, there are no bands in the region of 940–980 cm^{-1}, which would indicate the formation of a polymer. Thus, the downshift of the $A_g(2)$ mode in fullerene peapods is caused predominantly by charge transfer. In other words, because a formal charge transfer of 0.5 electrons per lithium atom is considered, the four electrons transferred to the fullerene cage correspond to eight lithium atoms per fullerene. On the other hand, for potassium-doped samples it has been shown that four atoms per fullerene penetrate the interior of the peapod.[2] The remaining two electrons per fullerene are believed to be balanced by the potassium atoms located outside of the peapod.[2] However, the lithium atoms are smaller than potassium atoms and therefore it is possible that more lithium atoms can be accommodated in the interior of a peapod.

An alternative explanation for the downshift of the $A_g(2)$ mode in lithium-doped peapods is the formation of a one-dimensional polymer or more effective charge transfer through the nanotube wall, which is less probable.

The fullerene bands in doped peapods are slightly asymmetric, but the broadening of the fullerene bands compared with the pristine peapod is almost negligible, which confirms the formation of a single-phase fulleride. The asymmetry of the fullerene bands of the fullerides is generally attributed to electron–phonon coupling.

Note also that similarly to potassium-doped samples,[17] the relative change in the intensity of the C_{60} bands does not resemble that of the tube related modes (RBM, TG). This is because different conditions exist for resonance enhancement in encapsulated fullerene C_{60} and in SWCNTs. For lithium-doped samples, the fullerene modes are most intense for 2.41 eV laser radiation, whereas for pristine samples the intensity of the fullerene mode reaches a maximum at 2.54 eV laser excitation (see Figures 1 and 2). This change in the resonance condition results in a different dependence of the $A_g(2)$ mode upon doping for the tested excitation laser energies: the $A_g(2)$ mode is slightly bleached upon doping with the 2.54 eV laser excitation energy, whereas it increases with the 2.41 eV laser excitation compared with the undoped peapod. In the latter case, the intensity increases by a factor of three in the doped sample compared with the undoped sample. With the 2.18 eV laser excitation energy, the $A_g(2)$ mode is not resolved in an undoped peapod, but it does appear in the spectra of the lithium-doped sample.

Water treatment: The lithium-doped samples were exposed to water vapor at 90 °C for 1 h to explore the stability of lithium fulleride inside the SWCNTs. The Raman spectra (excited by 2.54, 2.41, and 2.18 eV laser energy) of the treated peapods are shown in Figure 3. Water treatment leads to an increase in the intensity of SWCNT-related modes relative to those of the untreated lithium-doped samples. However, a more detailed analysis shows that the recovery of the

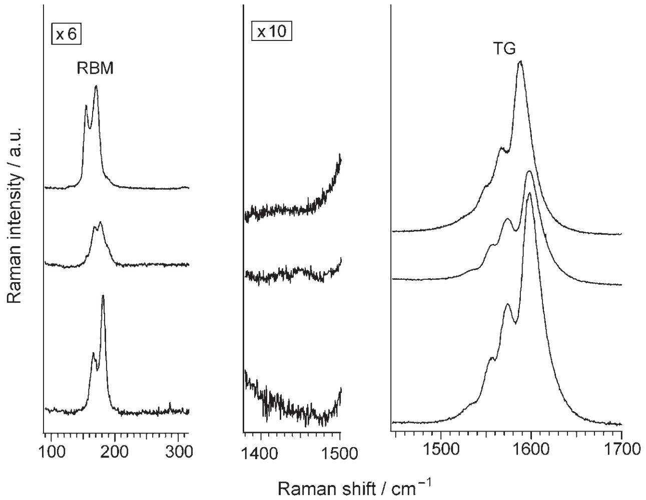

Figure 3. Raman spectra of lithium-doped C_{60}@SWCNTs after water treatment (excited at 2.18, 2.41, and 2.54 eV, from top to bottom). The intensities of the spectra were normalized by using the F_{1g} line of silicon at 520.2 cm^{-1}. The spectra are offset for clarity, but the intensity scale is identical for all the spectra in their respective windows.

spectral intensities is not complete. The final intensity of the TG band in water-treated lithium-doped samples is about 50–75 % smaller than that of the pristine (undoped) peapods. (The variation in the intensity measured at different spots on samples was typically around 5–20 % of the average value. Treatment with water had no significant effect on the intensity of the TG band of undoped samples.)

A similar deviation in the recovery of intensity is observed for the RBM. The band has a greater intensity after water treatment, but the original intensity of the pristine undoped sample is not recovered as well. Furthermore, there is a change in the shape of the RBM. For example, in the case of 2.41 eV laser excitation, a part of the RBM at 178 cm^{-1} is bleached to a larger extent than that at 168 cm^{-1}. An even more obvious change is observed for 2.18 eV laser excitation. Here a new band appears at 155 cm^{-1} in the doped and water-treated sample. This effect points to a change in the resonance condition as a consequence of residual doping of the peapod sample.

The most intense $A_g(2)$ band is expected to recover the position and intensity of the corresponding band of the pristine undoped peapods after water treatment of the lithium-doped sample. However, the intensities of the fullerene modes in the water-treated sample are very weak. This is similar to the spectroelectrochemical results obtained for pristine peapod samples for which the relatively low level of n-doping resulted in bleaching of the fullerene modes. Furthermore, in the case of 2.41 eV laser excitation, a maximum can be traced at 1450 cm^{-1}. This downshifted $A_g(2)$ band is also indicates excess negative charge on the fullerene cage.

The observed differences in the Raman spectra of pristine and water-treated doped peapods indicate that the sample remains partially doped even after water vapor treatment. The observed effects can be explained by the presence of lithium inside the peapod. This is because exposure to air/oxygen and humidity eliminates lithium doping outside the peapod wall, but it does not remove the lithium from the interior of the peapod. Our data are in qualitative accordance with the results obtained for potassium-doped peapods.[28] As the interactions of lithium with both SWCNTs and the fullerenes inside the nanotubes are strong due to the small ionic radius and the special properties of the lithium–carbon bond,[10,29] they could be similar to those in fullerenes prepared by the bombardment of C_{60} by lithium.[29]

In situ spectroelectrochemistry: The Raman spectra of lithium-doped peapods after water treatment indicated residual doping. For potassium-doped peapods it has been shown that it is possible to "de-dope" a sample by applying anodic electrochemical charging.[2] Similar effects of anodic charging are expected for lithium-doped peapods. To test the hypothesis, in situ Raman spectroelectrochemical measurements were taken (Figure 4). Raman spectroelectrochemistry of lithium-doped peapods after water treatment at different electrode potentials was followed from −1.8 to 1.2 V (vs. Fc/Fc$^+$). To avoid uncontrolled changes in the doping state, the measurements were started at −0.3 V (vs. Fc/Fc$^+$), which is close to the open circuit potential of a freshly assembled spectroelectrochemical cell. Subsequently, the potential was moved to −1.8 V and then to +1.2 V (vs. Fc/Fc$^+$; (Figure 4).

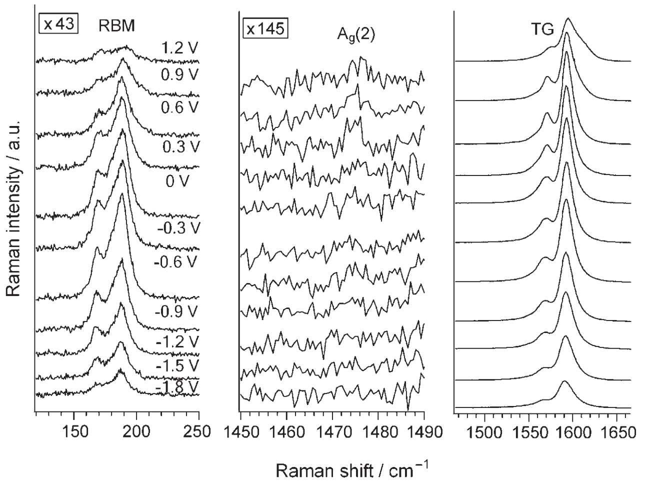

Figure 4. Potential-dependent Raman spectra (excited at 2.41 eV) of lithium-doped C_{60}@SWCNTs after water treatment on a platinum electrode in a 0.2 M $LiClO_4$/acetonitrile solution. The electrode potential was varied in steps of 0.3 V from 1.2 to −1.8 V (vs. Fc/Fc$^+$; curves from top to bottom). The spectra are offset for clarity, but the intensity scale is identical for all the spectra in their respective windows.

Cathodic charging, which is equivalent to weak lithium doping, leads to slight increases in the intensity of the nanotube-related bands and subsequently to continuous attenuation of these bands. Except for the initial increase in intensity, this resembles electrochemical doping of the pristine sample.[3] The bleaching of the nanotube bands caused by cathodic doping is a consequence of the filling of the conduction-band Van Hove singularities due to a shift of the Fermi level. This is an effect analogous to that of chemical doping, as discussed above. The reason for the initial increase in the Raman intensity is not yet clear. The negative electrode potential applied to the peapod attracts the (now hydrated) Li^+ ions. These lithium ions are both inside and outside of the peapod. This can lead to a redistribution of electrons in a lithium-doped peapod sample and compensate for the influence of intratubular lithium ions on the Raman spectra. The bleaching of SWCNT-related bands is very weak at the beginning of doping and thus the effect of the Li^+ ions can dominate. The final RBM intensity at -1.8 V (vs. Fc/Fc^+) is approximately 10 % of the original intensity of the doped and water-treated sample at 0 V (vs. Fc/Fc^+). The TG mode exhibits a decrease to approximately 20 % of its original intensity on going from 0 to -1.8 V (vs. Fc/Fc^+). This is also in good agreement with our previous data on pristine C_{60}@SWCNTs.[3]

The behavior of the TG band frequency of the peapods during electrochemical charging has been shown to be sensitive to the presence of the intratubular dopant.[2,4,9] The TG band of undoped pristine samples exhibits a shift to higher frequencies at elevated anodic potentials. The upshift of the TG band is about 15 cm^{-1} on going from 0 to $+1.2$ V (vs. Fc/Fc^+). Samples with an intratubular dopant do not exhibit an upshift of the TG band, but the band splits into two components, one of them dependent and the other independent of the electrode potential.[2,9] Nevertheless the effect is not yet fully understood.

As demonstrated in Figure 4, the in situ Raman spectroelectrochemical data point to the presence of lithium inside the peapod. Indeed, the TG band shows a more complex response to anodic potentials than the TG band of pristine peapods. The lithium-doped peapod exhibits a splitting of the TG band into a component with a higher frequency and a potential-independent component (Figure 4, upper curves on the right panel). This behavior is typical for situations in which the chemical dopant is located inside the carbon nanostructure.[9] Thus the spectroelectrochemical data confirm that the lithium dopant is located inside the carbon nanostructure.

We suggest that in the case of a lithium-doped peapod the effects caused by a positive electrode potential are compensated by the increased electron density on the fullerene cage, which is arrested by the presence of a counterion inside the peapod. The splitting of the TG band can be caused by the presence of two types of lithium ions, nonhydrated and partially hydrated ones. (The nanotube wall might be damaged by lithium doping and thus some water molecules can penetrate inside the peapod and interact with the fulleride.)

The intensities of the fullerene modes of lithium-doped peapods were very weak at the beginning of electrochemical doping. Even the most intense fullerene band, the $A_g(2)$ mode, was not distinguishable at the off-cell potential. The band also remained unresolved during cathodic charging of the lithium-doped peapod. Cathodic doping led to bleaching of the $A_g(2)$ mode in pristine samples (not shown). Thus it is not surprising that no change in the region of the $A_g(2)$ mode could be observed.

However, during anodic doping a band at 1470 cm^{-1} starts to appear, which is 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.[30] The "anodic Raman enhancement", first observed by us in pristine C_{60}@SWCNTs,[3,30] was also reproduced in potassium-doped peapods.[2] Here, we observe the enhancement effect for lithium-doped peapods, which indicates that the sample was p-doped by electrochemical charging (Figure 4). Our results are in agreement with a recent theoretical prediction for Li@C_{60} that the charge of fullerene can be changed without influencing the charge on lithium.[31]

Note that lithium vapor doping can damage the nanotube wall. This may lead to the decrease in the intensity of the $A_g(2)$ mode observed at high anodic potentials. Thus the observed enhancement of the intensity of the $A_g(2)$ mode can be suppressed.

Hence the in situ spectroelectrochemical data confirm the formation of the exohedral metallofullerene peapod and its electronic properties can be further tuned by electrochemical doping.

Conclusions

We prepared and studied lithium fulleride (C_{60}) peapods by Raman spectroscopy and spectroelectrochemistry. The initial high level of chemical doping was demonstrated by the disappearance of the RBM band, the dramatic reduction of the TG band, and the changes in the positions of the fullerene modes. The stability of the exohedral metallofullerene peapod was tested by exposing the sample to water vapor at 90 °C. Water treatment did not lead to complete recovery of either the tube's Raman modes or the fullerene bands. This indicates that in the reaction of the peapods with gaseous lithium the alkali metal is inserted not only between bundles, but also into the interior of the tube, to form an exohedral metallofullerene peapod, which results in a very stable metallofullerene structure. The material formed has characteristic spectral features including a lower intensity of the RBM and the TG bands of the SWCNTs and also of the $A_g(2)$ fullerene mode. The changes in the electronic structure of the fullerene in peapods induced by lithium vapor doping can be compensated and/or changed by electrochemical anodic doping. This was confirmed by in situ Raman spectroelectrochemical measurements. It was found that the $A_g(2)$ fullerene mode appears during electrochemical doping and slightly increases in intensity as the potential increases to high anodic values. In other words, chemical doping leads to the insertion of lithium in the carbon nanotubes, which is responsible for the downshift of the $A_g(2)$ mode, whereas electrochemical doping induces a charge at the fullerene indirectly through the doping of the nanotube wall. The position of the TG band of the lithium-doped and subsequently water-treated samples was independent of the applied electrochemical potential. This confirms the presence of an intratubular dopant in the lithium-doped and water-treated peapods.

Experimental section

Samples of the C_{60}@SWCNTs peapods (filling ratio of 85 %) were available from our previous work.[30] For chemical doping, the C_{60}@SWCNTs samples were outgassed at 285 °C/10^{-5} Pa (the residual gas was helium) and subsequently exposed at 473 °C to lithium vapor for 8 h. The reaction took place in a stainless steel ampoule interconnected to a Raman optical cell with a Pyrex glass window. Some of each lithium-doped C_{60}@SWCNTs sample was heated in water at 90 °C for 1 h to remove lithium from the voids between individual peapods.

A thin-film electrode was prepared by evaporation of a sonicated (sonication time $\approx$15 min.) ethanolic slurry of water-treated lithium-doped C_{60}@SWCNTs samples on the platinum 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 glove box. The cell was equipped with a platinum counter electrode and a silver wire pseudoreference electrode. $LiClO_4$ (0.2 M) as the supporting electrolyte was used in dry acetonitrile as the electrolyte solution. After the spectroelectrochemical measurements ferrocene (Fc) was added to the solution and the potential of the Fc/Fc^+ couple was measured for adjustment of the quasi-reference electrode. The potentials measured in reference to the silver pseudoreference electrode were recalculated and referenced to the Fc/Fc^+ couple. All electrochemical experiments were carried out in a three-electrode system using a PG 300 (HEKA) or an EG&G PAR 273A potentiostat.

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 1–5 mW). The samples were excited by an Ar^+ laser at 2.41 and 2.54 eV and a Kr^+ laser at 2.18 eV (Innova 305, Coherent). The Raman spectrometer was calibrated before each set of measurements by using the F_{1g} line of silicon at 520.2 cm^{-1}.

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