

Reversible Hole Engineering for Single-Wall Carbon Nanotubes

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Experimental results are provided for reversible generation of holes on single-wall carbon nanotubes and their closing by temperature treatment. The generation of the holes was analyzed by checking the amount of C₆₀ fullerenes that can be filled into the tubes and subsequently transformed to an inner-shell tube. The concentration of the latter was determined from the Raman response of the radial breathing mode. The tube opening process was performed by exposure of the tubes to air at elevated temperatures. This process was found to be independent from the tube diameters. In contrast, the tube closing process was found to depend strongly of the tube diameter. For large diameter tubes ($d = 1.8$ nm) the activation energy was 1.7 eV whereas for the small diameter tubes this energy was only 0.33 eV. Optimum conditions for tube closing were found to be one hour at 800 °C or 10 minutes at 1000 °C. From the almost identical Raman spectra for the tubes before and after engineering, a predominant generation of the holes at the tube ends is concluded.

Keywords: Single-Wall Carbon Nanotubes, Raman Spectroscopy, Filling of Nanotubes, Peapods, Purification, Controlled Oxidation, Diameter Control.

1. INTRODUCTION

The inside of carbon cages has been attracting the interest of chemists and physicists ever since the discovery of the fullerenes in 1985 by Kroto et al.¹ To develop an endohedral or concave chemistry was one of the dreams of the scientists in the early days of fullerene research. New materials and new chemical reactions, which do not exist outside the cages, were expected to be discovered. It was indeed demonstrated in a large number of experiments that atoms or even groups of atoms can be engaged into the fullerenes^{2–4} and revealed so far unobserved systems. However, a reversible opening, filling and re-closing of the cages was not possible. Only very recently such a process was demonstrated to operate for the filling of a fullerene cage with hydrogen atoms.⁵ In contrast to this, filling of carbon nanotubes had been demonstrated already in 1994⁶ shortly after the discovery of the tubes.⁷ At that time, filling of multi-wall carbon nanotubes was studied in some detail. Since the inner diameter of such tubes is rather large, of the order of 10 to 20 nm, fillers such as lead

or iron was expected and was observed to behave almost like bulk material. The situation changed when Smith et al. discovered the filling of single wall carbon nanotubes (SWCNTs) with C₆₀ fullerenes⁸ by electron beam irradiation. The resulting structures were called peapods. Shortly later it was reported by several groups that different types of fullerenes, including higher fullerenes or endohedral fullerenes can be filled into the SWCNTs^{9–11} if the tubes were treated in a special way in order to generate holes in the side walls or to open the caps of the tubes. The filling of the SWCNTs attracted considerable attention, since the inner diameter of the tubes is at least an order of magnitude smaller than the inner diameter of the multi-wall tubes and reaches values where quantum confinement becomes noticeable. Also, the highly shielded inside of the tubes were demonstrated to provide clean room conditions where highly defect free material can be grown.¹² Special recipes were reported for efficient filling but it turned out that any cleaning of the as grown tube material by chemical etching allows for filling with fullerenes or other inorganic or organic material. Attractive forces between the fullerenes and the inside of the cages were considered as the driving mechanism for the filling process. However, details of the

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filling mechanism remained not understood so far. Model calculations were able to demonstrate that the fullerenes can enter the tubes through holes in the side walls¹³ but filling from the tube ends seems also possible, and even more likely, since after the etching procedure there are natural holes of large enough size.

The filling process was reported to be less efficient if the tubes were annealed at moderate temperatures before the filling procedure, at least as far as filling with fullerenes is concerned. Partial or complete closing of the holes was considered as the reason for such behavior. Since the growth of nanomaterials within the one-dimensional nanospace inside the tubes is of fundamental interest, we report in this paper on a detailed study of the opening and closing processes for the SWCNTs. To do this, we make use of another interesting property of the fullerenes inside the tubes. At rather high temperatures of the order of 1400 K the fullerenes can be fused to a second tube, inside the master tube.^{14,15} These inner tubes exhibit an unusual strong Raman spectrum for the radial breathing mode¹² and therefore serve as a very sensitive probe of whether the filling was successful or not.¹⁶ The inner shell tubes are interesting by themselves as they have a very small diameter of the order of 0.7 nm, which implies rather strong deviation of structural and electronic properties from a flat graphene sheet. Applying the analytical technique of C₆₀ transformation we found critical temperatures where tubes with holes generated from a chemical treatment start to close. Such temperatures were found to depend on the diameter of the tubes. Small diameter tubes close first with a much lower thermal activation. In contrast, the opening of the tubes occurs with only a weak dependence on the diameter. Reversible closing and reopening is demonstrated.

2. EXPERIMENTAL DETAILS

SWCNTs were purchased from Med Chem Labs with a nominal diameter of 1.4 nm and a purity of 50%. Raman analysis revealed a Gaussian diameter distribution with peak value and width (variance) of 1.45 nm and 0.1 nm, respectively. The tubes could be filled with C₆₀ fullerenes as purchased by tempering them at 600 °C in a sealed and evacuated quartz tube for two hours together with excess amounts of C₆₀. Outside fullerenes were removed by dynamic vacuum annealing at 800 °C. This filling procedure was used throughout in the work presented here and will be called standardized filling in the following. After filling, the C₆₀ could be detected inside the tubes by Raman scattering and high-resolution transmission electron microscopy. However, neither technique allows for a diameter selective detection of the filling process. In order to obtain information on the latter, the peapods were transformed to double wall carbon nanotubes by tempering in high vacuum at 1250 °C for two hours and subsequent

slow cooling in the furnace. This procedure of inner shell tube growth from the peapods was used throughout in this work and will be assigned as standardized transformation in the following. The transformed material was then checked by Raman spectroscopy in the range of the radial breathing mode (RBM) for double wall carbon nanotubes (DWCNTs). Since the Raman response in the diameter range of the inner shell tubes is highly diameter selective, this yields diameter selective information on the filling process.

All Raman experiments were carried out at liquid nitrogen temperature with a Dilor xy triple spectrometer in the normal resolution mode, unless indicated otherwise. Detection of scattered light was performed with a blue enhanced and back-thinned CCD chip. For the excitation various laser lines were used in the red and yellow spectral range. Scattering intensities were evaluated as peak intensities of the Raman lines.

Annealing of as purchased or opened tubes was performed at various temperatures between 800 °C and 1200 °C in a sealed and evacuated quartz tube at a rest gas pressure of 10⁻⁶ Pa. Opening of the tubes was performed by exposure to air at various temperatures between 350 °C and 500 °C.

3. RESULTS AND DISCUSSION

Figure 1 depicts the Raman spectrum of DWCNTs in the spectral range of the RBM as obtained from a filling of pristine tubes and standardized transformation. The broad and only weakly structured line around 180 cm⁻¹ represents the response from the outer tubes. The group of narrow lines extending from 250 cm⁻¹ to 400 cm⁻¹ originates from the RBM of the inner shell tubes. According to our present understanding, each peak represents one tube or at least one pair of inner and outer tubes. Due to the low spectral resolution used, the well known splitting of the lines¹⁷ is not or only hardly resolved.

In the lower part of the figure the resulting diameter distribution is depicted on a $1/d$ scale. The narrower peak for the smaller $1/d$ -values was obtained from the Raman analysis of the diameter distribution of the outer tubes. The broad peak for the larger $1/d$ -values was obtained from a down scaling of the outer tube diameters by 0.7 nm which is considered as twice the relevant wall to wall distance between inner and outer tubes. The cut-off at 440 cm⁻¹ (0.5 nm diameter) reflects the limiting diameter value of 1.2 nm below which outer tubes cannot be filled with C₆₀ due to geometrical constraints. The relative scaling between the x -axis for the frequencies and the x -axis for the inverse diameters was obtained from the frequency to diameter scaling of the form

$$\nu_{\text{RBM}} = \frac{C_1}{d} + C_2 \quad (1)$$

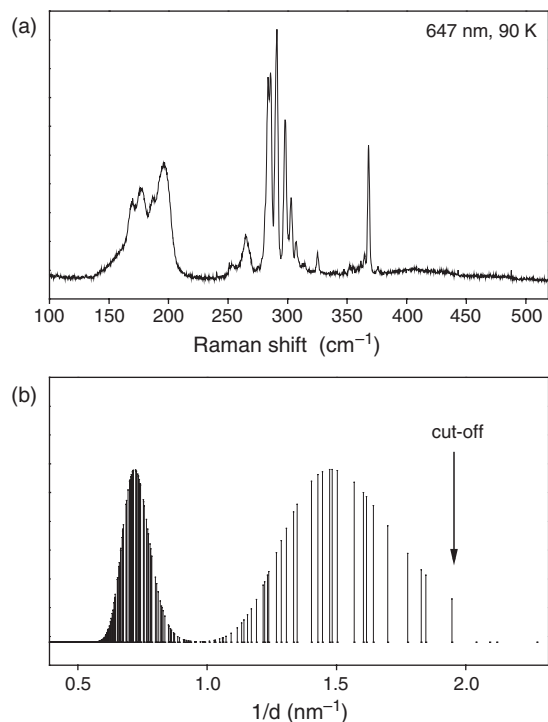


Fig. 1. Raman spectrum of DWCNTs as prepared from pristine SWCNTs filled with C_{60} (a). Excitation was for 647 nm laser and 2 mW. Part (b) of the figure displays the concentration of the diameters d on a $1/d$ scale.

where C_1 and C_2 have the values $223 \text{ cm}^{-1} \text{ nm}$ and 13 cm^{-1} , respectively. These parameters were recently obtained from a detailed analysis of resonance Raman excitations of HiPCo SWCNTs dispersed in solution.¹⁸ The values differ slightly from previous results obtained from a pure vibronic analysis of DWCNTs¹⁹ but are in good agreement with parameters obtained from an analysis of optical spectra and resonance Raman spectra from HiPCo tubes.^{20,21} Note the difference of the center of gravity for the $1/d$ distribution and for the Raman line distribution for both the inner tubes and the outer tubes. This is a consequence of resonance enhanced scattering for selected tubes. Comparing the peak intensities in the spectrum and in the $1/d$ distribution yields an enhancement factor >100 .

Figure 2 shows the Raman response of tubes after standardized transformation conditions but different pre-treatment. Only the spectral range of the inner tube is depicted in the main part of the figure. The spectrum at the bottom is an expanded version of the spectrum in Figure 1. The spectrum at the center was recorded under identical conditions but the as purchased material was pre-annealed before the standardized filling and standardized transformation. As can be seen almost no response from inner shell tubes is observed which means no fullerenes had entered the tubes. The tubes were very efficiently closed by the annealing process.

The small response just below 300 cm^{-1} could originate from some small leaks in the cage were a few C_{60}

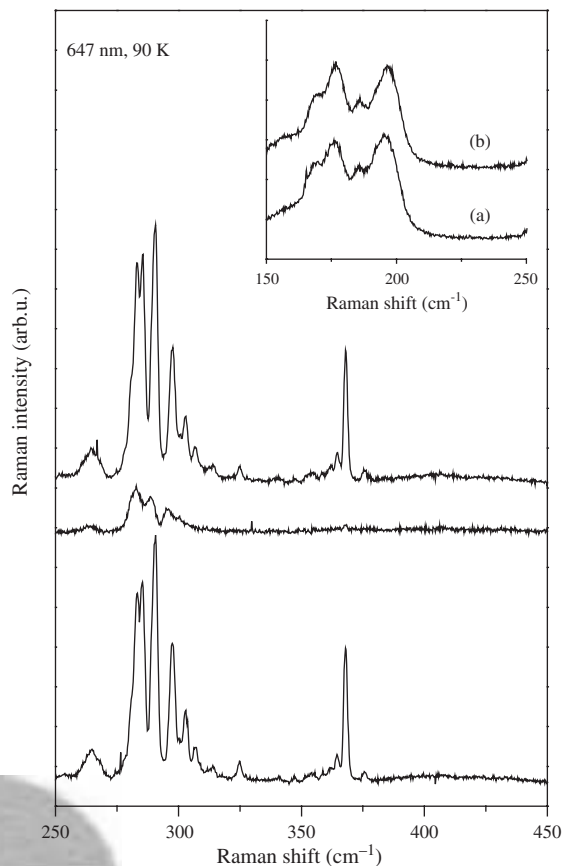


Fig. 2. Raman spectra in the spectral range of the inner shell tube RBM for nanotubes after special pre-treatment. Bottom: after filling as purchased tubes with C_{60} and standard transformation; Center: after annealing the as purchased tubes at $1000 \text{ }^\circ\text{C}$ for two hours and standard transformation; Top: after re-opening the annealed samples, filling with C_{60} , and standard transformation. All spectra recorded at 90 K for 647 nm , 2 mW excitation, 30 minutes sampling, and normalized to the response of the outer tube RBM of the pristine tubes. Insert: the RBM of the outer tubes before (a) and after (b) annealing at $1000 \text{ }^\circ\text{C}$.

molecules or even more likely some carbon contamination had entered the primary tubes on a level which leads to less than 20% inner tubes for the larger diameter tubes and less than 3% for the smaller diameter tubes. Also, these tubes were not grown under clean room conditions as the width of the Raman lines is rather broad. The insert in the figure depicts the RBM response from the outer tubes before and after annealing. The two spectra are almost identical which indicates that no tube coalescence had occurred at the temperature applied. The similarity of the two spectra allows on the other hand for a convenient way of intensity calibration for the spectra recorded after various sample pre-treatments. This calibration was used throughout the work presented here if not otherwise specified. The spectrum at the top in Figure 2 was recorded after reopening the annealed tubes at $500 \text{ }^\circ\text{C}$ on air and standard filling and transformation. As can be seen, the spectra derived from the pristine and from the reopened tubes are identical in all details. This means no dramatic damages by cutting

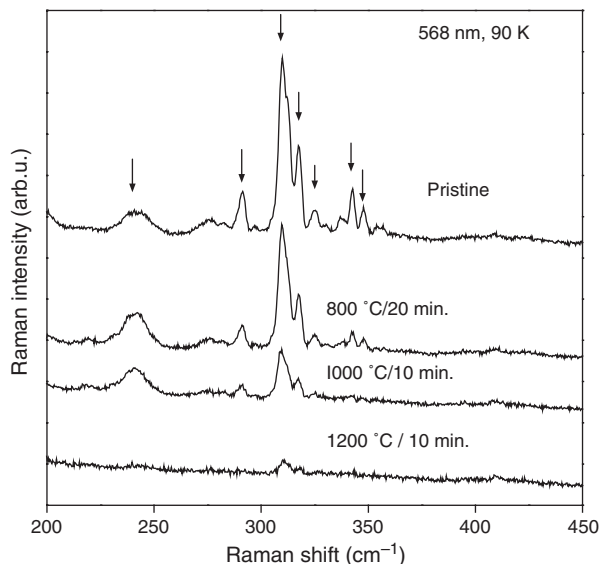


Fig. 3. Raman response of the inner tube RBM of the untreated and standardized filled and transformed tube material (top) and after various annealing treatments as indicated before the filling and transformation processes. All spectra recorded at 90 K for 568 nm, 2 mW excitation, 30 minutes sampling, and normalized to the response of the outer tube RBM of the pristine tubes. The arrows assign Raman peaks which were used for a detailed analysis shown in Figure 4.

a large number of holes into the sidewalls have happened. Consequently, the sidewalls of the tubes remain highly untouched by the opening process. Thus, it is strongly suggested that the fullerenes enter the tubes through holes at the tube ends.

Figure 3 depicts some examples for the efficiency of the tube closing for various annealing conditions. All spectra were now recorded with 568 nm excitation. The top spectrum represents the pristine tubes after standard filling and standard transformation. The three spectra below depict the response of the inner tube RBM for samples which were annealed under the conditions indicated in the figure before filling and transformation. As can be seen 800 °C annealing has almost no effect on the filling for the large diameter tubes but efficiently reduces filling of the smaller tubes with RBM frequencies larger than 300 cm^{-1} .

After 20 minutes annealing, the signal at 340 cm^{-1} has reduced to 35% of the signal of the pristine sample. This means 65% of this particular tube species was closed by the annealing process. After 10 minutes annealing at 1200 °C only a very small response from the inner shell tubes (less than 10% at 310 cm^{-1}) is left which again may be interpreted as the response from a small fraction of carbon atoms entering the tubes during the annealing process.

The dependence of tube closing on annealing temperature and time was studied in more detail. Spectra for the RBM response were recorded for standard filling and standard transformation after various annealing temperatures and annealing times. The most important lines were evaluated with respect to their peak intensity. This intensity was

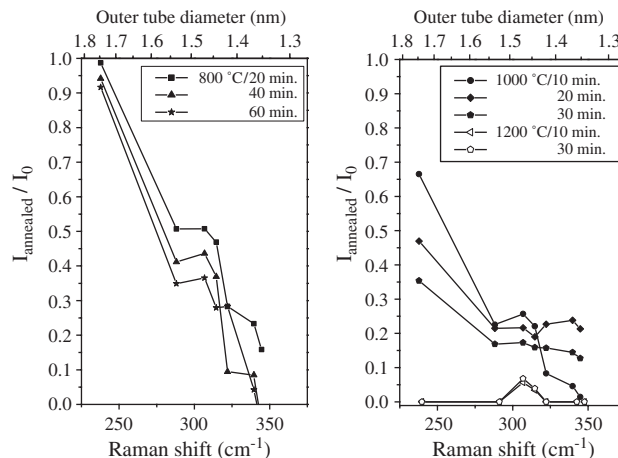


Fig. 4. Relative intensities I_{annealed}/I_0 of RBM Raman lines of the inner tubes versus frequency (tube diameter) after various annealing conditions as indicated in the inserted legend. All spectra were recorded and normalized as in Figure 3. The scale below the main figures gives tube diameters from Eq. 1.

related to the peak intensity of inner shell modes of DWC-NTs grown from untreated starting material. This ratio is a quantitative measure for the fraction of tubes which remain open after the annealing procedure. Results are depicted in Figure 4 for annealing at 800 °C (1073 K), 1000 °C (1273 K) and 1200 °C (1473 K). A dramatic decrease of concentration for tubes remaining open after the annealing treatment is immediately recognized on Figure 4 with decreasing tube diameter (increasing RBM frequency).

For tubes with 1.8 nm diameter (240 cm^{-1}) 98% remain open for a 20 min annealing at 800 °C whereas for the same annealing conditions and tubes with 1.3 nm diameter (345 cm^{-1}) only 15% remain open. A similar dramatic dependence of the tube closing on the tube diameter can be recognized for annealing at 1000 °C even though in this case after 10 minutes the concentration of open tubes has already decreased to 67% even for the largest diameter tubes studied. From the smallest diameter tubes analyzed only 2% remain open under these conditions. The strong temperature dependence of the tube closing process can be recognized from the behavior of the large diameter tubes. For the species with 240 cm^{-1} RBM the values are 98% and 47% after 20 minutes annealing at 800 °C and 1000 °C, respectively. This indicates a strong thermal activation of the closing process. The closing as a function of annealing time can also be deduced from the figure. With increasing annealing time, the process of tube closing proceeds but slows down as annealing time increases. This is particularly obvious for annealing at 1000 °C. Interestingly, for annealing at 800 °C the intensity ratios for the different annealing times always decrease with annealing time throughout the frequency range studied, with some noise at high frequencies. This is not so for annealing at 1000 °C. Here the annealing isotherms recorded for different annealing times cross as a function of RBM frequency (tube diameter). As a consequence, short time annealing

is more efficient for the narrow diameter tubes than long time annealing. For example for 1000 °C annealing the fraction of tubes with 345 cm⁻¹ RBM that remain open after 10 min, 20 min, and 30 min are 2%, 22%, and 14%, respectively.

For 1200 °C annealing any response from inner shell RBM for very large and very small tubes remains below the detection limit which is of the order of 1%. Only in the intermediate diameter range a very small and annealing time independent signal from inner shell tubes could be detected.

Finally, the analytical technique developed here can also be used to study the diameter selective tube opening process. Figure 5 depicts Raman spectra of the RBM recorded for 647 nm excitation for tubes which were closed at 1000 °C for two hours and then reopened by exposure to air at temperatures indicated.

As an overall result, the opening process becomes less and less efficient with decreasing temperature. However, the reduction in efficiency is hardly depending on the tube diameter. The latter behavior is more evidently seen from an analysis of the response for the individual peaks as

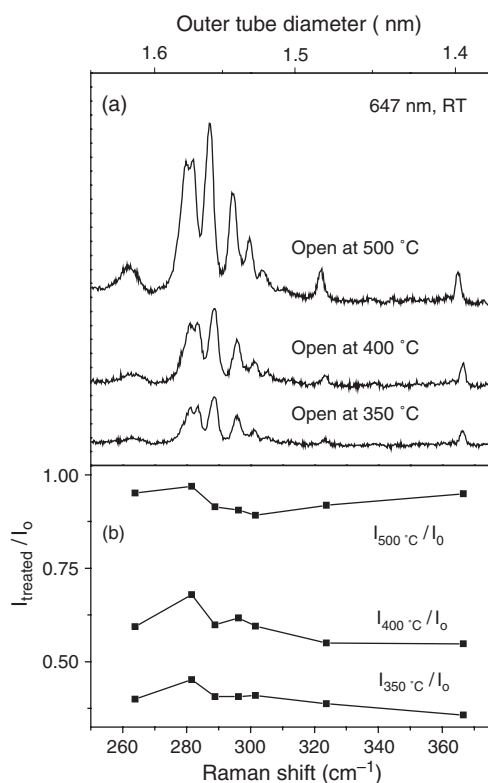


Fig. 5. Raman response of the RBM of inner shell CNTs for standard filling and transformation procedures after the pristine tubes had been closed and reopened at temperatures indicated (a). Part (b) depicts evaluated relative intensities versus Raman shift for the three different opening conditions. I_0 is the intensity for the pristine tubes after standard filling and transformation. The scale below the main figure provides tube diameters from Eq. 1. All spectra recorded at RT for 647 nm, 2 mW excitation, 30 minutes sampling, and normalized to the response of the outer tube RBM of the pristine tubes.

depicted in part (b) of Figure 5. For opening at 500 °C 95% of the closed tubes could be reopened, nominally independent of tube diameter. For opening at 400 °C only about 60% of the tubes could be opened. Surprisingly, as plotted this fraction is even slightly decreasing with decreasing tube diameter. Similarly, for opening at 350 °C only 45% of the tubes could be opened again, with a slight decrease of this fraction for small diameter tubes.

The analytical technique used here anticipates that the Raman intensity for the RBM of a particular inner shell tube equals the concentration of the tube in the sample. This is justified, since for each measurement exactly the same resonance conditions and spectrometer sensitivity hold and all spectra are normalized to the RBM response of the outer shell tube.

Concerning the closing of holes which are required to allow the fullerene molecules to enter, three main results were obtained, namely:

- (i) The closing process is thermally activated with an increasing efficiency for low diameter tubes.
- (ii) The closing process is time dependent with saturation for long annealing times.
- (iii) For small diameter tubes the time dependence of the effective closing is more complex.

Result (iii) makes the analysis of the dynamical processes more difficult for the small diameter tubes. Thus, for the discussion of the thermal activation and for the time dependence we will concentrate on the large and medium diameter tubes. The temperature dependence of the closing process is indeed dramatic. Note that for a change in temperature of only 18% (from 1073 K to 1273 K) the closing fraction for the tubes with a RBM at 240 cm⁻¹ ($d = 1.78$ nm) after 20 minutes annealing changes by a factor of more than 25. The activation energy α for this process can be evaluated from

$$\alpha = k_B T_1 T_2 \frac{\ln \left[1 - \frac{I(T_1)}{I(T_2)} \right]}{(T_1 - T_2)} \quad (2)$$

where k_B is the Boltzmann constant and $I(T)$ are the relative intensities from Figure 4. For $T_1 = 1073$ ($I(T_1)/I_0 = 0.98$) and $T_2 = 1273$ ($I(T_2)/I_0 = 0.67$), we obtain $\alpha = 1.72$ eV. If we do the same analysis for a medium diameter tube, e.g., with an RBM at 285 cm⁻¹ ($I(T_1)/I_0 = 0.52$, $I(T_2)/I_0 = 0.23$) the activation energy is only 0.33 eV. This value may be slightly underestimated, since for medium diameter tubes secondary processes to be discussed below start to become noticeable. For still smaller diameter tubes the activation is obviously further reduced but cannot be analyzed directly due to other competing processes. The dramatic decrease of the activation energy with tube diameter must be a consequence of tube wall or tube cap curvature and higher mobility of carbon atoms on the tube surface.

Similar to the thermal activation, the time dependence of the closing process may be described by an exponential

Table I. Experimental data and relaxation time τ for the tube closing process at 1273 K and two selected tube diameters. The concentrations for open and closed tubes after 120 min (1.8 nm diameter) and 60 min (1.45 nm diameter) annealing is as calculated for 26 and 8 min time constants, respectively.

d [nm]/ RBM [cm^{-1}]	Annealing time [min]	Open tubes [%]	Closed tubes [%]	Time constant [min]
1.8/240	10	0.67	0.33	25
	20	0.47	0.53	26
	30	0.35	0.65	28
	120	0.01	0.99	Calc. for $\tau = 26$
1.45/305	10	0.26	0.72	7.5
	20	0.22	0.78	13.2
	30	0.17	0.83	17
	60	5×10^{-4}	~ 1	Calc. for $\tau = 8$

law with a relaxation time τ obtained from

$$\frac{I(t)}{I_0} = \exp\left(\frac{-t}{\tau}\right) \quad (3)$$

where $(I(t))/I_0$ is the fraction of open tubes after annealing time t .

Table I lists some of the experimental results for 1000 °C annealing at 240 cm^{-1} and 305 cm^{-1} . For the tubes with the largest diameters (1.8 nm) evaluation of the time constants for the three different annealing times reveal values in good agreement, which supports the exponential time dependence. For the averaged time constant of 26 minutes a two hour annealing at 1000 °C would leave only 1% of the tubes open.

As expected for the smaller tubes with $d = 1.45$ nm (RBM at 305 cm^{-1}) the evaluated time constants are much shorter. The value of about 8 minutes may still be all right but for longer annealing times secondary processes obviously influence the evaluated time constant. The value of about 13 min for a 20 minutes annealing process is noticeably larger than the value for ten minutes annealing. It even increases to 17 min for 30 min annealing. Therefore the latter values should not be considered as intrinsic for the tube closing process. The much shorter time constants for the closing of the smaller diameter tubes is again a consequence of the higher tube curvature and consistent with the lower activation energy.

The increase of the time constant for tube opening or eventually the crossing of the annealing isotherms for different annealing times is surprising. One possibility to describe such a behavior is by proposing two processes with complimentary effects on the hole-concentration in the tubes. One process is responsible for the hole-closing and the other with a considerably larger time constant generates holes into the tube walls or tube caps. Then, only for long time annealing the opening process becomes relevant. The opening process could e.g., be a very slow reaction of the tubes with rest gas concentration of oxygen in the annealing experiment. For a quantitative analysis of the behavior more detailed results are needed.

The results for the tube opening as a function of tube diameter and reaction temperature in Figure 5 must be analyzed with some care. It would be very difficult to understand why small diameter tubes open less efficient than large diameter tubes as one might conclude from the low temperature (350 °C and 400 °C process temperatures) reactions depicted in Figure 5. For a more realistic interpretation we can assume that the starting situation for the tube opening process is not the same for the large diameter tubes and the small diameter tubes. The former may not have closed completely by the annealing process whereas the smaller diameter tubes have. Such a behavior can be depicted from the 30 minutes annealing at 1000 °C shown in Figure 4. The annealing isotherm shows that for the small diameter tubes still 15% remain open. The effect is, however, weakened by the slow tube opening process noticeable for small diameter tubes. Even though, with the corrected starting situation at least the opening reaction at 500 °C may be more sensitive to the smaller diameter tubes. In spite of these corrections the tube opening processes are definitely much less sensitive to the tube diameter as compared to the tube closing processes. The thermodynamic background for this different behavior may be related to the fact that tube opening is a very local process whereas tube closing needs long distance carbon motion and long distance carbon rearrangements. After all for a small tube almost 50% of the side wall or the total cap must be etched away in the opening process and at least partly replaced by the closing process.

4. SUMMARY

The reaction activity of holes in SWCNTs was investigated by studying the process of filling the tubes with C_{60} fullerenes and transforming the latter to a set of small diameter inner shell tubes. A standardized process for tube opening by exposing the tubes at elevated temperatures to air and for tube filling by heating the opened tubes in C_{60} vapor was developed. The process of tube opening was found to be sensitive to temperature but highly insensitive to tube diameter. The almost identical Raman spectra for the pristine and for the opened tubes with respect to line positions, line widths and line intensities suggest that the tube walls remain highly untouched and the holes for the tube filling are concentrated at the tube ends. Tube closing can be performed to a very high degree. After such processes, only a very small amount of inner tubes can be grown, mostly in high defect areas of the tubes. In contrast to tube opening, the tube closing process is highly diameter sensitive with a strongly diameter dependent activation energy and a temperature dependent reaction time. A reversible closing and opening of the tubes was demonstrated.

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References and Notes

1. H. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* 318, 162 (1985).
2. Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford, and R. E. Smalley, *J. Phys. Chem.* 95, 7564 (1991).
3. D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. de Vries, and C. S. Yannoni, *Nature* 366, 123 (1993).
4. H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando, and Y. Saito, *J. Phys. Chem.* 97, 4259 (1993).
5. K. Komatsu, M. Murata, and Y. Murata, *Science* 307, 238 (2005).
6. C. Guerret-Piécourt, Y. Le Bouar, A. Loiseau, and H. Pascard, *Nature* 372, 761 (1994).
7. S. Iijima, *Nature* 354, 56 (1991).
8. B. W. Smith, M. Monthieux, and D. E. Luzzi, *Nature* 396, 323 (1998).
9. K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H. Shinohara, and S. Iijima, *Phys. Rev. Lett.* 85, 5384 (2000).
10. K. Hirahara, S. Bandow, K. Suenaga, H. Kato, T. Okazaki, H. Shinohara, and S. Iijima, *Phys. Rev. B* 64, 115420 (2001).
11. T. Okazaki, K. Suenaga, K. Hirahara, S. Bandow, S. Iijima, and H. Shinohara, *J. Am. Chem. Soc.* 123, 9673 (2001).
12. R. Pfeiffer, H. Kuzmany, and C. Kramberger et al., *Phys. Rev. Lett.* 90, 225501 (2003).
13. D. Tomanek, private communication (2003).
14. S. Bandow, M. Takizawa, K. Hirahara, M. Yudasaka, and S. Iijima, *Chem. Phys. Lett.* 337, 48 (2001).
15. F. Simon, H. Kuzmany, H. Rauf, T. Pichler, J. Bernardi, H. Peterlik, L. Korecz, F. Fülöp, and A. Jánossy, *Chem. Phys. Lett.* 383, 362 (2004).
16. F. Simon, Á. Kukovecz, C. Kramberger, R. Pfeiffer, F. Hasi, H. Kuzmany, and H. Kataura, *Phys. Rev. B* 71, 165439 (2005).
17. R. Pfeiffer, C. Kramberger, F. Simon, H. Kuzmany, V. N. Popov, and H. Kataura, *Eur. Phys. J. B* 42, 345 (2004).
18. C. Fantini, A. Jorio, M. Sousa, M. S. Strano, M. S. Dresselhaus, and M. A. Pimenta, *Phys. Rev. B* 93, 147406 (2004).
19. Ch. Kramberger, R. Pfeiffer, H. Kuzmany, V. Zólyomi, and J. Kürti, *Phys. Rev. B* 68, 235404 (2003).
20. S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, and R. B. Weisman, *Science* 298, 2361 (2002).
21. H. Telg, J. Maultzsch, S. Reich, F. Hennrich, and C. Thomsen, *Phys. Rev. Lett.* 93, 177401 (2004).

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