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# Selective Etching of Thin Single-Walled Carbon Nanotubes

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***Abstract:*** Raman spectroscopy and in situ Raman spectroelectrochemistry were applied to study the selective etching of thin tubes by lithium vapor in doped single-walled carbon nanotubes (SWCNTs). A strong doping of SWCNTs after the reaction with Li vapor was confirmed by the vanishing of the radial breathing mode (RBM) and by a strong attenuation of the tangential displacement (TG) band in the Raman spectra. The Raman spectra of the Li-vapor-treated SWCNTs after subsequent reaction with water showed changes in the diameter distribution compared with that of a pristine sample (nanotubes with diameters of <1 nm disappeared from the Raman spectra). The samples were tested by the Raman pattern with five different laser lines, and a removal of narrower tubes was confirmed. The remaining wider tubes were not significantly damaged by the treatment with Li, as indicated by the D line in the Raman spectra. Furthermore, the small-diameter tubes are converted not into amorphous carbon but into lithium carbide, which could easily be removed by hydrolysis. The treated samples were further charged electrochemically. It was shown by spectroelectrochemistry that anodic charging may lead to removal of the residual chemical doping from the thicker nanotubes in the sample, but the thin nanotubes did not appear in the spectra. This is a further confirmation of the removal of the small-diameter tubes.

## 1. Introduction

The sorting of single-walled carbon nanotubes (SWCNTs) is still a challenging task. Significant achievements have been reached using electrophoresis and density-gradient centrifugation.[1] However, these approaches can provide only a small amount of sorted nanotubes at the present time, and obviously, scaling up the method is difficult. Furthermore, the method requires isolated individual nanotubes to be used. This requirement adds two additional preparation steps to the separation of the nanotubes. First, surfactants must be added to the SWCNTs to detach the tubes from a bundle, and second, at the end of the process the surfactants must be again removed. Hence, for the sorting of a large amount of SWCNTs, chemical treatment is more promising. It should allow an easy scale-up without requiring individualization of tubes. Chemical treatment procedures have been drawn by nanoelectronics, which requires a separation of nanotubes with different electronic properties. It has been shown that metallic tubes can be selectively removed from the samples by treatment with diazonium salts[2] or nitronium[3] or by a combination of bromine doping and centrifugation.[4] However, the chemical methods still need to be improved. Chemical treatment usually leaves materials with a strong D line in the Raman spectra, indicating an abundance of defects in the nanotubes as well as formation of amorphous carbon,[3] which is difficult to remove.

Chemical treatment usually causes an additional doping of the carbon nanotubes. This may also lead to a misinterpretation of the results. For example, even reversible electrochemical charging erases the broadening of the TG mode in the Raman spectra.[5,6] Hence, in some cases the removal of the TG-mode broadening might be erroneously interpreted as a successful removal of metallic tubes from the sample.

The electronic structure of carbon nanotubes can be reversibly tuned by electrochemical treatment. This is important in nanoelectronics, since it has been shown that doping substantially influences the electronic properties of the nanotubes.[7,8] Furthermore, electrochemical doping can be used to remove an extra charge from chemically doped carbon nanostructures, as has been demonstrated for chemically doped fullerene peapods.[8,9] Hence, electrochemical treatment can be used to distinguish between charging and removal of metallic tubes.

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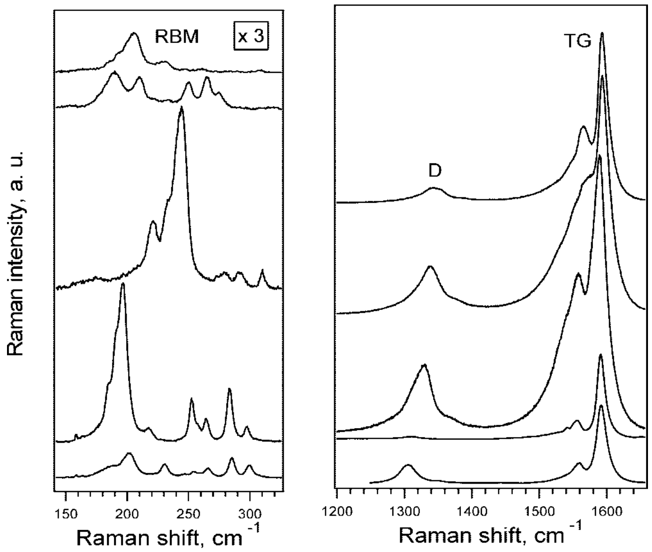

***Figure 1.*** Raman spectra of pristine SWCNTs excited at energies of 1.83, 1.92, 2.18, 2.41, and 2.54 eV (from bottom to top). Intensities were normalized using the $F_{1g}$ line of Si at 520.2 cm$^{-1}$. The spectra have been offset for clarity, but the intensity scales are identical for all of the spectra in their respective windows.

Lithium doping is attractive with respect to its application in charge storage. Therefore, several experimental and theoretical studies of Li doping of SWCNTs have appeared.[10−14] It has been demonstrated that the charge storage capacity of SWCNTs could be twice that of graphite.[15] However, most experimental studies have dealt with electrochemical doping in solution.[7] It has been shown by several examples that the doping mechanism is different in the cases of chemical and electrochemical doping.[8,9,16] Here we present a Raman spectroscopic study of Li-doped SWCNTs. Gaseous Li metal was used to dope the sample. To dedope the samples, they were treated with water vapor. The resulting material exhibited a different SWCNT diameter distribution than pristine samples, as small-diameter tubes were selectively removed. The removal is demonstrated by Raman spectroscopy using five different laser excitation energies. To the best of our knowledge, this is the first demonstration of a reductive removal of nanotubes from a mixture in general and of the application of Li vapor for this purpose in particular.

## 2. Results and Discussion

**2.1. Li Doping.** The Raman spectra of pristine SWCNTs excited by five different laser energies (2.54, 2.41, 2.18, 1.92, and 1.83 eV) show the RBM bands between 150 and 320 cm$^{-1}$ and the TG band at ~1595 cm$^{-1}$ (Figure 1). From the frequency of the RBM band ($\omega_{\mathrm{RBM}}$), one can determine the diameter ($d_t$) using eq 1:

$$\omega_{\mathrm{RBM}} = \frac{A}{d_t} + B \tag{1}$$

where $A = 217.8$ nm cm$^{-1}$ and $B = 15.7$ cm$^{-1}$.[17] Hence, the diameter distribution of the tubes in the studied sample is in the range 1.62−0.72 nm. The G$^{-}$ lines (low-frequency parts of the TG band) in the spectra excited by the 2.18 and 2.41 eV laser radiation exhibit broad Breit−Wigner−Fano (BWF) line shapes, indicating a dominant contribution of metallic tubes to the Raman scattering at these excitation energies. On the other hand, the G$^{-}$ line is not significantly broadened for the 1.83, 1.92, and 2.54 eV laser radiation, and thus, the semiconducting tubes are predominately in resonance at these laser energies.

The Raman spectra of Li-doped SWCNTs excited by the 2.54, 2.41, 2.18, 1.92, and 1.83 eV laser lines (Figure 2) demonstrate that the overall spectral intensity of the doped sample is considerably smaller than that of the pristine sample (Figure 1). The RBM band vanished almost completely, which proves the high level of doping.

The intensity of the TG band of the Li-doped sample is also very low compared with that in pristine samples (Figure 1). The decrease in the TG-band intensity upon doping is ~2 orders of magnitude at all laser excitation energies. The dramatic attenuation of the Raman intensities is generally explained by the doping-induced filling of the Van Hove singularities (VHs).[7] (As soon as the VHs are filled or depleted, the optical transitions between the particular singularities are erased. The optical transitions play a crucial role in the resonance enhancement of Raman spectra, and thus, filling of the VHs causes a suppression of the Raman signal.)

The frequency of the TG mode does not change significantly. This is contrary to our previous experiments on SWCNTs heavily doped with potassium vapor. In that case, the doping induced a strong downshift in the frequency of the TG mode.[16] Nevertheless, the behavior of the TG-band frequency of doped nanotubes is still under conflicting debate, especially for n-doping.[7] For SWCNTs, both frequency upshifts and downshifts have been reported, depending on the level of doping and the type of counterion used (Li$^{+}$, K$^{+}$, Rb$^{+}$, or Cs$^{+}$).[18−26] The detailed study by Chen at al.[25] showed that there are at least four stages of the doping procedure: (1) a long induction period,

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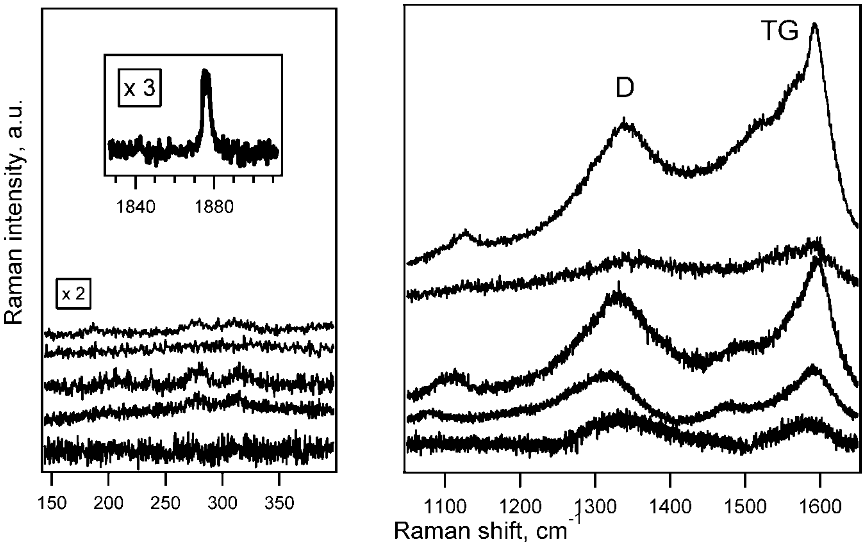

***Figure 2.*** Raman spectra of Li-doped SWCNTs excited at 1.83, 1.92, 2.18, 2.54, and 2.41 eV (from bottom to top). Intensities were normalized using the $F_{1g}$ line of Si at 520.2 cm$^{-1}$. The spectra have been offset for clarity, but the intensity scales are identical for all of the spectra in their respective windows. The inset shows a new band at 1875 cm$^{-1}$ in the Raman spectrum of Li-doped SWCNTs excited at 2.18 eV, which can be attributed to the C≡C acetylene bond of lithium carbide.

(2) a short interval during which the RBM and TG bands are bleached, (3) a slight upshift in 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.[27] Hence, the softening of the TG band is not expected for doped isolated SWCNTs. However, this contrasts with the experimental results, since a similar behavior of the TG band has been found for isolated nanotubes.[24] Consequently, other effects, such as structural disorder, hardening of the lattice via interactions of the tube or the alkali metal ion, and/or doping-induced renormalization of the phonon energy, must be considered.[28,29]

**2.2. Water Treatment.** The Li-doped samples were exposed to water vapor at 363 K for 1 h. The Raman spectra (excited by 2.54, 2.41, 2.18, 1.92, and 1.83 eV laser energy) of the water-treated Li-doped SWCNTs are shown in Figure 3. The water treatment causes an increase in the Raman intensities compared with those of the untreated Li-doped samples. However, a more detailed analysis showed that the recovery of the spectral intensities is not complete.

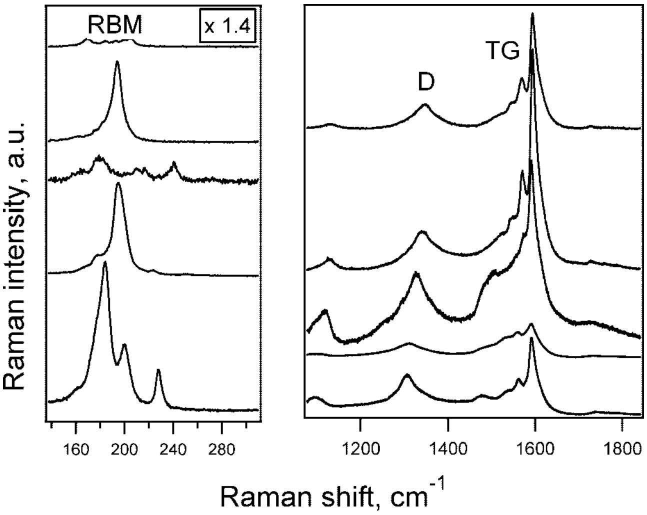

***Figure 3.*** Raman spectra (excited at 1.83, 1.92, 2.18, 2.41, 2.54 eV, from bottom to top) of Li-doped SWCNTs after water treatment. Intensities were normalized using the $F_{1g}$ line of Si at 520.2 cm$^{-1}$. The spectra have been offset for clarity, but the intensity scales are identical for all of the spectra in their respective windows.

The most striking difference is found in the RBM region. For example, the spectrum of pristine SWCNTs excited at 1.83 eV shows RBM bands at 300, 285, 265, 253, 230, and 201 cm$^{-1}$ with a shoulder at 185 cm$^{-1}$ (Figure 1). However, the spectrum of the sample after Li doping and water treatment exhibits only three bands at 228, 200, and 185 cm$^{-1}$ with a shoulder at 177 cm$^{-1}$ (Figure 3). Obviously, the four RBM bands at 300, 285, 265, and 253 cm$^{-1}$ present in the spectrum of pristine sample are missing in the spectrum of the Li-doped sample after water treatment. Similar changes were also found by comparison of the spectra of the pristine and Li-doped water-treated samples excited at 1.92, 2.18, 2.41, or 2.54 eV. Generally, all the bands above 240 cm$^{-1}$ disappeared as a result of Li doping and water treatment. According to eq 1, these tubes have diameters smaller than 1 nm. Furthermore, the relative intensities of the RBM bands at frequencies below 240 cm$^{-1}$ are changed, so that the spectra are dominated by lines of the tubes with large diameters.

The intensity of the TG band of the water-treated Li-doped samples is slightly smaller than that in pristine samples. The shape of the TG mode also exhibits some differences between the pristine samples and the Li-doped samples after the water treatment. For example, the TG mode of the water-treated Li-doped samples is broadened for the 1.92 eV laser excitation, indicating metallic tubes. However, such a broadening is missing for pristine samples.

The chemical treatment of SWCNTs usually causes a dramatic increase in the D mode intensity due to the increased

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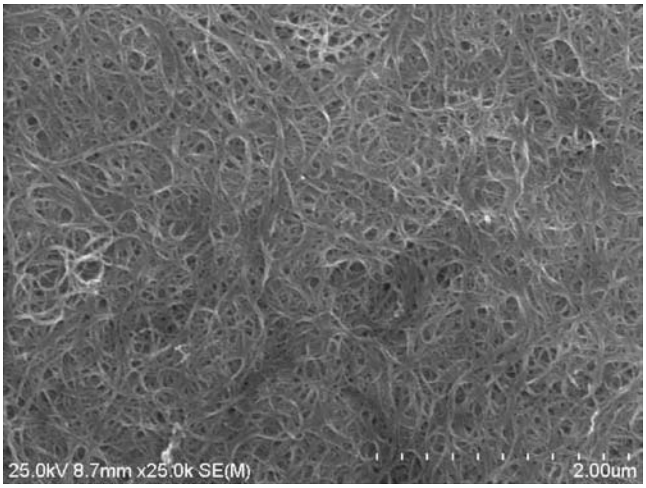

***Figure 4.*** SEM image of the Li-doped SWCNTs after washing with both 1 N HCl and water.

disorder.[3] However, for the Li-doped samples presented here, this is not the case. The D line is only slightly increased, i.e., the tubes remaining in the water-treated Li-doped sample were not significantly affected, and the amount of amorphous carbon was not increased. This effect is probably caused by the enhanced reactivity of the partly etched and/or defective nanotubes. This is also confirmed by the scanning electron microscopy (SEM) image in Figure 4, which shows the SWCNTs after treatment with Li for 22 h at 485 °C and washing with both 1 N HCl and water (see the Experimental Section). Control experiments (data not shown) confirmed that the treatment with HCl does not have any significant influence on the Raman spectra.

**2.3. In Situ Raman Spectroelectrochemistry.** To gain a deeper understanding of the observed effects of Li doping and water treatment on SWCNTs we performed in situ Raman spectroelectrochemical measurements. This study was motivated by our previous experience with fullerene peapods, which showed that chemical n-doping with Li or K vapor can be selectively erased by applying anodic electrochemical charging.[8,30] Similar effects of the anodic charging are expected for the Li-doped SWCNTs. The Raman spectroelectrochemistry of Li-doped SWCNTs after water treatment was followed at potentials from −1.5 to 1.5 V vs Ag (Figure 5). To avoid uncontrolled changes of the doping state, the measurements started at 0 V vs Ag. Subsequently, the electrode potential was moved to −1.5 V and then to +1.5 V vs Ag (Figure 5).

Cathodic charging, which is equivalent to weak lithium doping, leads to a continuous attenuation of the SWCNT features, which resembles what was observed for electrochemical charging of pristine sample.[7] The bleaching of nanotube bands caused by cathodic doping is a consequence of the filling of the conduction-band VHs because of the shift of the Fermi level. This effect is analogous to the chemical n-doping effect discussed above.

The final RBM intensity at −1.5 V vs Ag is less than 10% of the original intensity of the doped and water-treated sample at 0 V vs Ag. The tangential mode exhibits a similar decrease to ∼10% of its original intensity in going from 0 to −1.5 V vs Ag. This is also in good agreement with previous data on pristine SWCNTs.[5]

Anodic doping is expected to dedope the treated SWCNT samples. If there is a residual doping by Li, the excess electrons will be removed from the nanotube. Indeed, at potentials up to 0.6 V there is a small increase in the intensities of SWCNT features (the TG and RBM bands). However, increasing the doping level by treatment at positive potentials up to ∼0.6 V causes a strong bleaching of the bands, as observed for pristine samples. This follows the simple doping model, as the extensive doping leads to depletion of VHs, and consequently, the resonance effect is quenched.

It is important to note that only the RBM modes that are already present in the Raman spectra of the water-treated Li-doped sample increased in intensity. The RBM bands of narrow SWCNTs that were present in the pristine sample but not in the Li-doped sample after water treatment did not reappear, even when the sample was dedoped electrochemically at high anodic potentials. It is obvious that the quenching of the RBM bands of the thin tubes is not caused by residual doping. Instead, these tubes are indeed irreversibly decomposed by the reaction with Li.

The behavior of the TG band of the SWCNTs during electrochemical charging has been shown to be sensitive to the presence of the intratubular dopant.[8,9,16] The TG band of pristine samples shifts to higher frequencies at higher anodic potentials. The samples with an intratubular dopant do not exhibit an upshift of the TG band, but the band splits into two components, one of which is dependent and the other independent of the electrode potential.[8,16] Despite the fact that this effect is not fully understood, it can be used for a qualitative evaluation of the location of the dopant in carbon nanostructure samples.[16] For the water-treated Li-doped SWCNT sample under study, the TG mode is upshifted from 1592 to ∼1600 cm$^{-1}$ in going from 0 to +1.5 V vs Ag. This is similar to the behavior for the pristine sample. In other words, this finding confirms that the dopant is not present in the interior of the SWCNTs.

We suggest that the small-diameter tubes have been chemically destroyed by Li vapor. It is known that $Li_2C_2$ can be formed directly from the elements at high temperature. However, this reaction can occur at temperatures as low as 720 K,[31] while in our case, the Li doping was performed at 746 K. Hence, the SWCNTs can form the $Li_2C_2$ under our experimental conditions. Indeed, the Raman spectra of the Li-doped SWCNTs exhibit a new band at 1875 cm$^{-1}$ (inset of Figure 2) that can be attributed to the C≡C acetylene bond. This band is absent in the sample before doping and also disappears after the water treatment of the Li-doped sample. The $Li_2C_2$ is decomposed by water to form acetylene and LiOH. It is important that the product of etching of narrow tubes is not amorphous carbon, which would be difficult to remove. On the contrary, the final products (acetylene and LiOH) can easily be removed by washing with water or dilute acids. It should be noted that the formation of some amorphous carbon may be found for samples treated extensively with Li. This is probably due to the incomplete etching of more stable large-diameter tubes.

As demonstrated in Figures 1 and 3 and in detail in Figure 6, only narrow tubes can be etched. The narrow nanotubes are usually considered to be more reactive than wider ones. The curvature of graphene decreases the stability of carbon−carbon bonds. This has been observed previously, for example, in the

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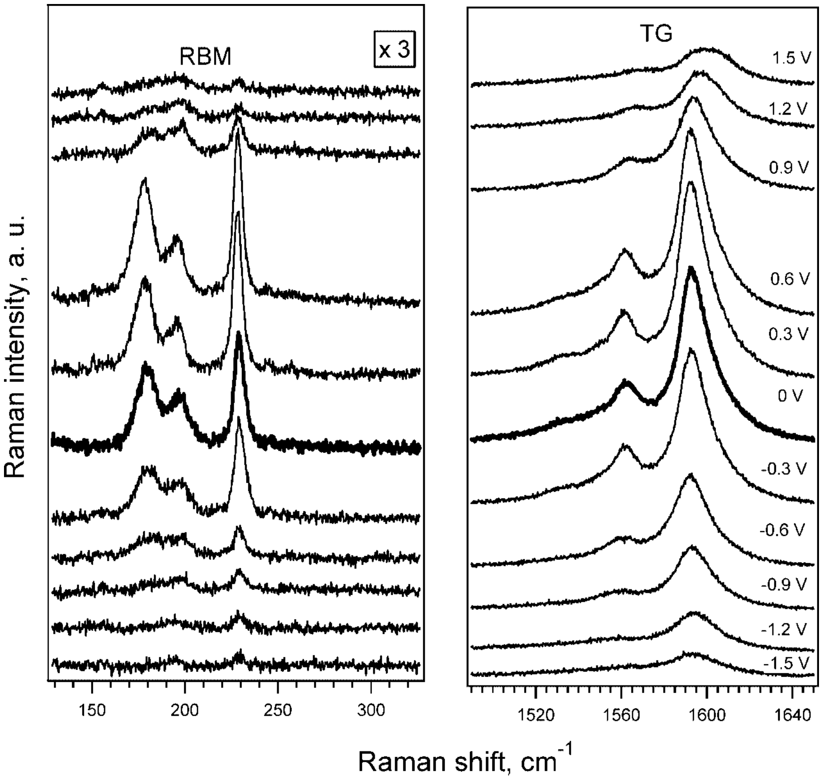

***Figure 5.*** Potential-dependent Raman spectra (excited at 1.83 eV) of the Li-doped SWCNTs after water treatment on a Pt electrode in 0.2 M $LiClO_4$/acetonitrile solution. The electrode potential was varied in steps of 0.3 V from 1.5 to −1.5 V vs Ag (curves from top to bottom). The spectra have been offset for clarity, but the intensity scales are identical for all of the spectra in their respective windows.

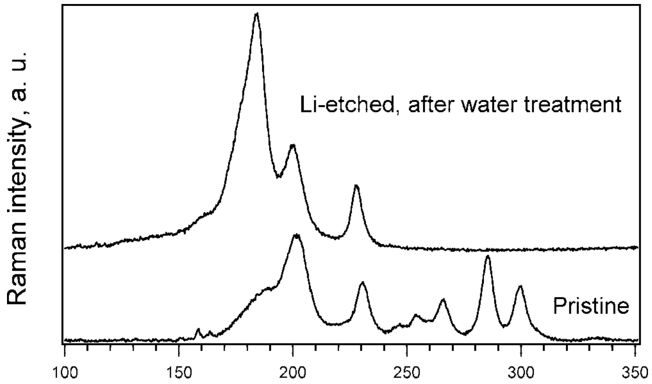

***Figure 6.*** Comparison of the Raman spectra of pristine and Li-etched SWCNTs after water treatment. The spectra were excited at 1.92 eV, and their intensities were normalized using the RBM mode at ∼195 cm$^{-1}$. The spectra have been offset for clarity.

reaction of SWCNTs with nitronium ions.[3,32] We assume that the greater reactivity of narrow tubes is the reason for their selective removal in our experiments.

The removal of narrow tubes obviously results in a change of the environment of the wide tubes. It has been shown previously[33] that the environment has a significant impact on SWCNTs and their spectral properties. Hence, the changes in the Raman spectra of the wide tubes can be rationalized.

## 3. Conclusions

Selective etching of thin carbon nanotubes by Li vapor was revealed by Raman spectroscopy and in situ Raman spectroelectrochemistry. The initial high level of chemical doping was demonstrated by the vanishing of all of the Raman features of the SWCNTs. The Li-treated SWCNTs were dedoped by exposing the sample to water vapor at 363 K. It was found that only the features of SWCNTs with diameters greater than 1 nm remain in the Raman spectra of the water-treated Li-doped sample. In situ Raman spectroelectrochemical measurements indicated that the large-diameter tubes can be further dedoped by anodic charging. The RBM bands of the thin tubes did not reappear, even in the spectra of electrochemically dedoped samples. This indicates that the small-diameter tubes were etched by Li vapor to form $Li_2C_2$. Furthermore, the position of the TG band of the Li-doped and subsequently water-treated samples was found to upshift with increasing positive electrode potential, which confirms that Li is not present inside the SWCNTs. The reaction of Li vapor with SWCNTs can be used as a cheap, scalable, and clean method for the removal of small-diameter tubes.

## 4. Experimental Section

The sample of SWCNTs (HiPco) was available from our previous work.[34] For the chemical doping, the SWCNT samples were outgassed at 558 K/10$^{-5}$ Pa (the residual gas was He) and subsequently exposed to lithium vapor at 746 K for 8−22 h. The reaction took place in a stainless-steel ampule interconnected to a Raman optical cell with Pyrex glass windows. A portion of the

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Li-doped SWCNT sample was heated in water vapor at 363 K for 1 h to dedope the sample. For SEM observations, the sample was additionally rinsed with 1 N HCl, since we found that this treatment is more efficient for removal of the products of the $Li_2C_2$ decomposition.

A thin-film electrode was prepared by evaporation of a sonicated (sonication time ~15 min) ethanolic slurry of the water-treated Li-doped SWCNT sample on a Pt electrode in air. The film electrode was outgassed overnight at 363 K in vacuum ($10^{-1}$ Pa) and then mounted in a spectroelectrochemical cell in a glovebox. The cell was equipped with a Pt counter electrode and a Ag pseudoreference electrode. $LiClO_4$ in dry acetonitrile (0.2 M) was used as the electrolyte solution. All of the electrochemical experiments were carried out in a three-electrode system using a HEKA PG 300 or EG&G PAR 273A potentiostat.

Raman spectra were measured on a T64000 spectrometer (HORIBA Jobin Yvon) interfaced to an Olympus BH2 microscope (the laser power impinging on the sample or cell window was 1−5 mW). Spectra at 2.41 and 2.54 eV were excited by an $Ar^+$ laser and those at 1.83, 1.91, and 2.18 eV by a $Kr^+$ laser (Innova 305, Coherent). The Raman spectrometer was calibrated before each set of measurements using the $F_{1g}$ line of Si at 520.2 $cm^{-1}$.

SEM images were obtained using a Hitachi FE SEM S-4800 microscope.

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