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Temperature effects in the Raman spectra of bundled single-wall carbon nanotubes

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ABSTRACT

Bundled single-walled carbon nanotubes (SWCNTs) were studied as a function of temperature by means of Raman spectroscopy. The Raman modes exhibit negative temperature shift, reversible for the G band and partially irreversible for the radial breathing modes (RBMs). The softening of the latter is larger for larger diameter tubes, resulting in a better separation of the RBMs after high temperature treatment (HTT). The RBM residual softening *vs.* treatment temperature demonstrates threshold-like behavior. The temperature-induced changes may be associated with an irreversible weakening of the tube–tube (intertube) interaction possibly due to adsorbent removal or destruction of random intertube C–C bonds.

1. Introduction

The effects of temperature on bundled SWCNT were studied experimentally by X-ray diffraction and Raman spectroscopy [1–5]. The temperature dependence of the nanotube diameter, the expansion of the bundle lattice and the intertubular spacing due to the lattice anharmonicity were studied in detail by X-ray diffraction [1]. The absolute value of the thermal expansion coefficient deduced for the tube diameter was very small, while the thermal expansion coefficient of the lattice constant was relatively large, so that the intertube expansion coefficient is larger than the thermal expansion coefficient of graphite in the *c*-axis direction [1]. Another X-ray diffraction study has revealed the important role of various adsorbents in the temperature behavior of bundled SWCNTs [2]. The temperature dependence of the bundle lattice constant of the purified SWCNTs differs for the first heating and cooling cycles, where shrinkage of the SWCNT bundles was observed. During the second and subsequent temperature runs, temperature dependencies similar to that of the cooling cycle of the first run were observed. After exposure of the samples in the atmosphere, the temperature dependence becomes again similar to that of the first heating cycle. The observed peculiarities were explained assuming temperature-induced removal of adsorbents, which are present in the interstitial channel sites or inside the nanotubes due to the high adsorption ability of bundled SWCNTs to the atmospheric N_2 and O_2 gases [6].

The temperature shift of the RBM and the G band in bundled single- and double-walled carbon nanotubes was studied by Raman spectroscopy at temperatures up to 800 K [3–5]. The Raman study and molecular dynamics simulations of bundled HiPCO SWCNTs have attributed the negative temperature shift of the RBM and the G band mainly to the softening of the C–C intratubular bonds and the van der Waals intertubular interaction [3]. The thermal expansion of tubules in the radial direction does not contribute appreciably in the temperature shift, as suggested by the small expansion value obtained from the molecular dynamics simulations [3]. This result is consistent with X-ray diffraction studies that suggest even negative temperature expansion of the tube diameter [1].

The important feature of carbon nanotubes is their ability to aggregate in bundles and special techniques are required for their separation in individual tubes, like the ultrasonic exfoliation of SWCNT bundles in water-surfactant dispersions [7]. The strong intertubular bonding is due to high cohesive energy of the van der Waals interaction, which is a few times higher than that of the C_{60} fullerene molecules for equivalent tube length [8]. Taking into account the typical high length of nanotubes, the total van der Waals interaction between tubes becomes very strong, resulting in the formation of bundles – closed packed nanotubes arranged in a hexagonal lattice. Additional reason for strong bonding of nanotubes in the bundles may be their interlinking via C–C intertubular bonds [9]. Carbon nanotubes have a potential for creation of these bonds due to a large number of unsaturated double C=C bonds, similar to the case of C_{60} fullerite where its polymerization takes place after illumination or high pressure/high temperature treatment [10–12]. Numerical calculations predict one- and two-dimensional networks of interlinked SWCNT, some of which are energetically more stable than the hexagonal lattice formed through van der Waals interaction [13]. The interlinking of nanotubes assumes their deformation in the radial direction that requires the application of high pressure [13]. An experimental

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study of the high pressure/high temperature treated SWCNTs shows irreversible changes in their structure and Raman spectra, providing evidence for covalent interlinking through sp^3 C–C bonds [14]. One can not also exclude the random interlinking of nanotubes at ambient conditions caused by light illumination similarly to the photopolymerization of C_{60}. On the other hand, the treatment of the fullerene polymers at temperatures higher than ~550 K causes their depolymerization that result in irreversible changes of their structure and optical spectra [15–17]. Similarly, the high temperature treatment of bundled SWCNTs may show irreversible changes related to the breaking of the random C–C bonds if the nanotube interlinking really takes place. In view of this, we investigated the Raman spectra of purified SWCNTs as a function of temperature by means of *in situ* micro-Raman spectroscopy. We find that the temperature shift of the RBM frequencies is partially irreversible, resulting in a residual softening of the RBM frequencies. The softening is larger for large diameter tubes, whereas its dependence on the treatment temperature exhibits a threshold-like character. We discuss the possible reasons of the observed effects in terms of the temperature-induced removal of adsorbed atmospheric gases and/or destruction of the tube interlinking caused via random C–C bonds.

2. Experimental

The starting SWCNT material was synthesized by the arc discharge evaporation method in helium atmosphere at a pressure of 0.86 bar using a metallic Ni/Y catalyst. The purification method, based on the multistep oxidation in air and reflux in HCl, resulted in a ~90 wt.% content of SWCNTs. The average diameter of the SWCNTs was 1.5 nm (1.4–1.6 nm), as it follows from the preparation method, transmission electron microscopy (TEM) and Raman characterization. No surfactants were applied during the purification procedure. The final material was a black fluffy powder that consisted of large (~100 μm) nanotube mats with high optical activity [18]. The main impurities were graphite nanoparticles in the order of 2–4 μm, while the total content of metal impurities was ~1.3%. The final product was annealed in vacuum at 873 K for 5 h.

Raman spectra from small SWCNT pieces with typical dimensions of 100 μm were recorded *in situ* in the back-scattering geometry using a micro-Raman setup comprised of a triple monochromator (DILOR XY) and a CCD detector system, cooled at liquid nitrogen temperature. The 514.5 nm line of an Ar$^+$ laser was focused on the sample by means of a 20× objective in a spot of ~3 μm diameter, while the beam intensity on the sample was ~1 mW. For the high temperature measurements, a home-made high temperature cell with a temperature controller that maintained temperatures up to 750 K with an accuracy of ±2 K was used.

3. Results and discussion

The Raman spectrum of the purified bundled SWCNTs recorded at ambient conditions in the regions of the RBM and the G modes is shown in Fig. 1a. The D band, not shown in the figure, is weak and its intensity is ~1% of the integrated intensity of the G band. The relatively narrow peaks and the small integrated intensity of the D band are typical of structurally ordered SWCNTs. The occurrence and the dispersive behavior of the D band in graphite-related materials are associated with structural disorder while a double-resonance process was employed for their interpretation [19]. The intense G band at a higher energy corresponds to the tangential C–C stretching vibrations perpendicularly (G^- component, the most intense peak is centered at ~1568 cm^{-1}) and parallel (G^+ component, centered at ~1591 cm^{-1}) to the axial direction of a semiconducting SWCNT. The shape of the G^- component is sensitive to the electronic properties of SWCNTs. In our case, the Lorentzian lineshape of the G^- component indicates that the probed SWCNTs are semiconducting, whereas a Breit-Wigner Fano lineshape is typical for metallic SWCNTs [20]. The low frequency band related to RBM is comprised of a prominent peak at 170 cm^{-1}, and shoulders at ~179 cm^{-1} and ~160 cm^{-1}, respectively. The RBM frequency, ω_R, is inversely proportional to the tube diameter, d_t, while its value is upshifted due to the intertube interaction within the bundle [20]. One of the empirical relations between d_t and ω_R, applicable for bundled SWCNTs is [20]:

$$d_t(\text{nm}) = \{234\ \text{nm cm}^{-1}\}/\{\omega_R(\text{cm}^{-1}) - 12\ \text{cm}^{-1}\} \qquad (1)$$

According to Eq. (1), the main RBM peak at 170 cm^{-1} corresponds to SWCNTs with diameters of ~1.48 nm, whereas the shoulders at 160 and 179 cm^{-1} correspond to SWCNTs with diameters of ~1.58 nm and ~1.40 nm, respectively. Fig. 1b and c show the Raman spectra after high temperature treatment of the SWCNTs at 530 K and 630 K, respectively, recorded at the same conditions as in Fig. 1a. The frequencies of the RBMs after HTT are shifted to lower energies: the mode softening is higher for larger tube diameters and increases with the increase of the treatment temperature, which results in better separation of the RBM peaks. The HTT does not affect the G modes and the frequencies of the G^- and G^+ components do not change within the experimental resolution.

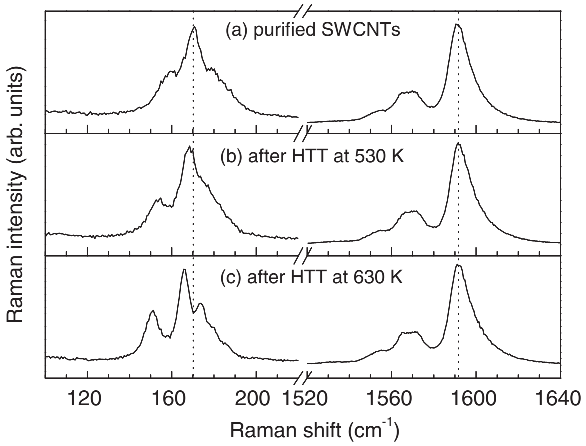

Fig. 1. Raman spectra in the RBM and the G band frequency regions of (a) purified SWCNTs, (b) SWCNTs after HTT at 530 K and (c) SWCNTs after HTT at 630 K. All spectra are recorded at the same sample site and at ambient conditions.

The temperature dependence of the RBM frequencies, obtained by fitting Lorentzian peak functions to the Raman spectra, is illustrated in Fig. 2 for three different temperature runs (circles, squares and triangles). The results of the heating (cooling) temperature cycles are indicated by open (solid) symbols. The Raman spectra of the heating cycles were measured with a step of 25 K. The increase of temperature and its stabilization at the new value takes ~20 min, while the accumulation time was ~50 min. During the cooling cycles, measurements where recorded at step of ~50 K, while longer time was required for thermal stabilization due to the relatively large mass and thermal inertia of the temperature cell. The open and solid circles in Fig. 2 clearly show the irreversible temperature dependence of the RBM frequencies and their residual softening after the first temperature run (temperature range: 300–430 K). Squares in Fig. 2 show the temperature dependence of the RBM frequencies obtained during the second temperature run. The Raman spectra were recorded at the same sample site. The second run – starting at room temperature- focuses in the temperature re-

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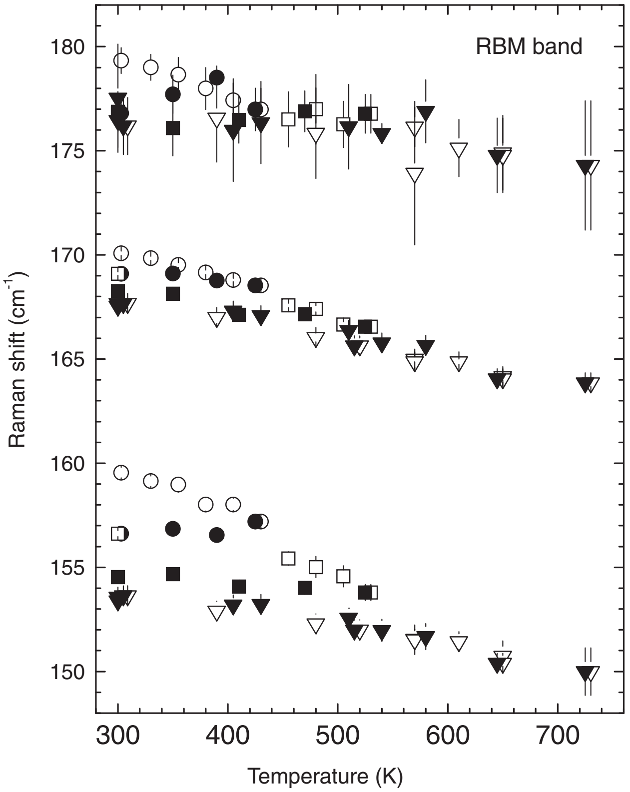

Fig. 2. Temperature dependence of the RBM peak frequencies of the bundled SWCNTs. Open (solid) symbols correspond to heating (cooling) cycles. Circles refer to the first temperature run (300–430 K), squares to the second temperature run (300–530 K) and triangles to the third temperature run (300–730 K).

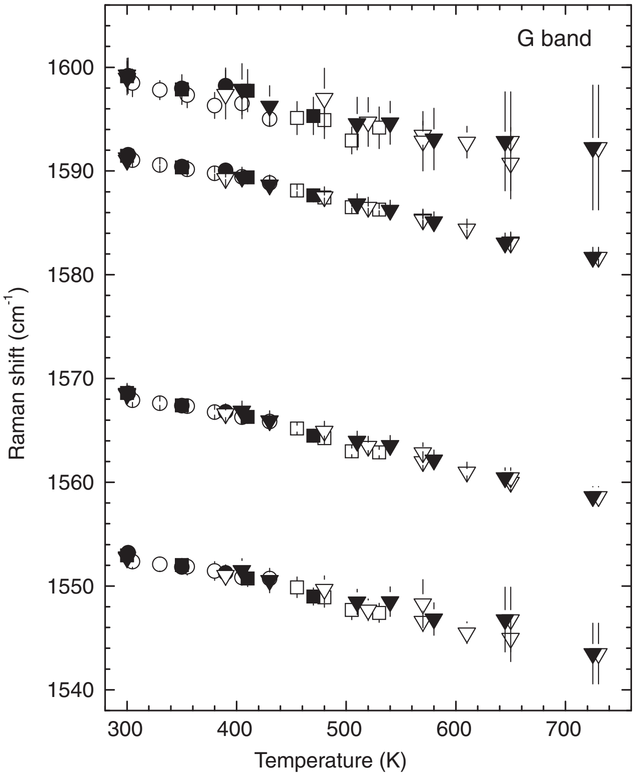

Fig. 3. Temperature dependence of the G band peak frequencies of the bundled SWCNTs. Open (solid) symbols correspond to heating (cooling) cycles. Circles refer to the first temperature run (300–430 K), squares to the second temperature run (300–530 K) and triangles to the third temperature run (300–730 K).

gion 455–530 K, extending the temperature range of the first run. The temperature dependence of the RBM frequencies in the second temperature run is also irreversible and shows further softening of the RBMs. The residual softening is diameter dependent, being smaller for smaller tube diameters, while for the smallest ones (highest RBM frequency) it is practically zero within the experimental resolution. Finally, the third temperature run, performed in the temperature range 300–730 K, is reversible within the accuracy of the measurements and no further residual softening of the RBMs is observed (triangles in Fig. 2). The temperature dependence of the G band peak frequencies is shown in Fig. 3. The circles, squares and triangles correspond to data recoded at the same sample site during the three temperature runs mentioned above. The temperature dependence of the frequencies, unlike that of the RBMs, is fully reversible within the accuracy of the measurements. We note also, that the frequency of the D band and its intensity relative to the G band before and after HTT (up to 730 K) remain essentially unaffected (not shown), suggesting that the structural quality of the SWCNTs is not altered by the HTT.

In order to study in detail the residual softening of the RBMs under various HTT conditions, we measured the Raman spectra of the purified SWCNT samples in a number of independent temperature runs. The residual softening of the RBMs (frequency difference) was determined from the room temperature Raman spectra measured before and after HTT for $\sim$20 min at temperatures up to 730 K. Both spectra were recorded at the same site of the sample, which was changed to a new one for each HTT. The dependence of the RBM softening on the treatment temperature is shown in Fig. 4. The open and closed circles correspond to the RBMs related to SWCNTs with diameters $\sim$1.48 nm and $\sim$1.58 nm, respectively. The residual softening is very small for treatment temperatures up to $\sim$430 K. At higher treatment temperatures, the softening rapidly increases, tending to its maximum value above 530 K. Further increase of the treatment temperature does not result in a significant increase of the RBM softening. The residual softening exhibits a threshold-like character and increases abruptly in the temperature interval 430–530 K. Note that, after the HTT the observed softening of the RBM frequency is preserved at least for 2–3 days after sample exposure at ambient conditions.

The most interesting effect in the temperature behavior of the Raman spectra of bundled SWCNTs is this threshold-like dependence of the RBM softening on the treatment temperature. The softening of the RBMs may be related to irreversible increase of the tube diameter and/or decrease of the intertube interaction near the threshold temperature. According to molecular dynamics calculations, the influence of the intertube van der Waals interaction on the vibrational spectrum of bundled SWCNTs was found to diminish with increasing phonon frequency, becoming negligible at phonon frequencies higher than 500 cm^{-1} [21]. Therefore, the influence of the intertube interaction on the G band frequencies is negligible, explaining their reversible temperature dependence irrespectively of any changes in the interaction potential. On the contrary, the influence of the intertube interaction on the RBM frequencies is relatively strong, resulting in their irreversible softening upon changes of the intertube interaction. Moreover, the influence increases with the decrease of the RBM frequency, resulting in a larger residual softening of the lower frequency RBM peak.

To clarify the nature of the irreversible temperature effects in bundled SWCNTs we have to analyze various effects that may cause irreversible changes in the intertube interaction and/or in the tube diameters after HTT. Firstly, regarding the tube diameter, its thermal expansion coefficient is almost zero, so the tube diameter can be considered unchanged under sample heating [1]. Note

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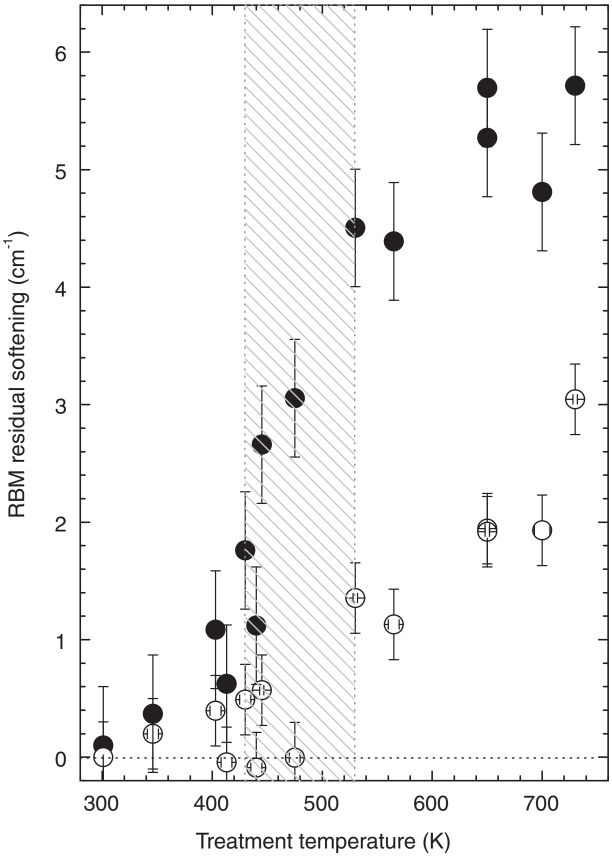

Fig. 4. Dependence of the residual softening of the RBM peaks on the treatment temperature. Open circles correspond to SWCNTs with diameters ~1.48 nm (RBM peak at 170 cm^{-1}), and solid circles to SWCNTs with diameters ~1.58 nm (RBM peak at 160 cm^{-1}).

that an irreversible increase of the tube diameter was observed due to the coalescence of nanotubes resulting in diameter-doubled nanotubes [22]. However, this followed after HTT at ~1800 K in a H_2 atmosphere -which is obviously not our case- and the softening related to the doubling of the nanotube diameter is expected to be considerably larger than that illustrated in Fig. 4.

Secondly, the irreversible changes in the intertube interaction after HTT may be caused by removal of adsorbed atmospheric N_2 and O_2 gases, which are usually present in the interstitial channel sites or inside the nanotubes due to the high adsorption ability of bundled SWCNTs [6]. It was found that the bundle lattice constant of purified SWCNTs decreases irreversibly from 17.1 to 16.9 Å after the first heating/cooling run due to the desorption of molecules from the intertube space of bundles when the sample is heated under vacuum [2]. The second and the following temperature runs do not exhibit any further change of the lattice constant, while after the sample exposure in the atmosphere, the temperature dependence becomes again similar to that of the first run. The radial shrinkage of SWCNT bundles takes place in the temperature region 300–600 K, similar to the observed irreversible changes in the Raman spectra presented here. It is interesting to note, that the decrease of the bundle lattice constant should result in the increase of the intertube interaction and the upshift of the RBM frequencies in contrast to our experimental observations. One may assume that the presence of adsorbed molecules in the interstitial channel sites of bundles results in an enhancement of the intertube interaction and their removal causes an overall decrease of interaction despite the intertube distance reduction. Unfortunately, there are no theoretical data related to the influence of adsorbents on the intertube van der Waals interaction in bundled SWCNTs. On the other hand, the softening of the RBMs may be related to the removal of adsorbents from inside the open-ended nanotubes as their interior is the primary adsorption site [6]. The encapsulation of various molecular species inside carbon nanotubes causes frequency shifts of their RBMs [23]. In our case, if adsorption results to a frequency upshift of the RBMs, similarly to the case of carotene encapsulating SWCNTs [24], then the observed RBM residual softening after HTT can be attributed to the desorption process.

Finally, the residual softening of the RBMs could be also related to an irreversible increase of the intertube distance caused by the destruction of random C–C bonds between the nanotubes after the HTT of bundled SWCNTs. The random interlinking of nanotubes – that may take place at ambient temperature conditions and light illumination – assumes a decrease of the mean intertube distance and local deformation of nanotubes in the radial direction near the bond. The HTT of bundled SWCNTs may result in the destruction of the C–C intertube bonds, similarly to those of the photo polymerized fullerene C_{60} or its high pressure/high temperature crystalline polymers [15–17]. The threshold-like character of the RBM softening on the treatment temperature with a threshold temperature in the region 430–530 K could be an indication of the destruction of the C–C intertube bonds if the interlinking of SWCNTs at ambient conditions really takes place.

The Raman data presented in this Letter clearly illustrate the irreversible changes in the intertube interaction of bundled SWCNTs caused by their treatment at high temperature conditions. The origin and the reasons of these changes in the intertube interaction are not quite clear yet and additional experimental investigations, e.g. by means of differential scanning calorimetry and time-dependent annealing experiments, or theoretical explorations would be required.

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