

Raman study of the high-pressure hydrogenated single-wall carbon nanotubes: In search of chemically bonded and adsorbed molecular hydrogen

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Abstract

Single-wall carbon nanotubes (SWNT) hydrogenated at $P \approx 5.0$ GPa and $T \approx 500$ °C (SWNT-H) were investigated by micro-Raman spectroscopy. The main feature of the Raman spectrum of the as-prepared SWNT-H is a giant structureless hot luminescence background that screens all vibrational modes. This disorder-induced background, attributed to random binding of the hydrogen atoms, vanishes after annealing of the SWNT-H in vacuum or in air. The changes in the Raman spectra of the partially annealed samples reflect the gradual decrease of structural disorder, related to removal of randomly bonded hydrogen. Complete outgassing restores the characteristic Raman spectrum of the pristine SWNT.

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1. Introduction

Carbon nanotubes are being widely investigated, among other reasons, for their hydrogen storage capability [1–4]. A good storage medium must have a high potential to adsorb high density of hydrogen. Molecular hydrogen can be either adsorbed inside the nanotubes constituting a nanotube bundle or it can fill the space between the tubes in the bundle [5]. In addition, hydrogen atoms can form covalent bonds with carbon atoms in a SWNT due to the existence of a large number of unsaturated double C=C bonds. For example, hydrogenation of the C₆₀ fullerene results in the formation of the stable C₆₀H₁₈ and C₆₀H₃₆ chemical derivatives, where hydrogen atoms are

covalently bonded to carbon [6–8]. Reported efficiencies of the hydrogen uptake in SWNT-H vary between 4 and 8 weight percent (wt.%) of both molecular and covalently bonded hydrogen. In view of this, the important problem is to distinguish the adsorbed molecular hydrogen from that of the covalently bonded one. Raman spectroscopy has been successfully used in the study of covalently bonded hydrogen in fullerene hydrides [8] as well as in the study of the molecular hydrogen physisorption on the ropes of SWNT [9]. In carbon-related materials, the covalently bonded hydrogen exhibits intense Raman peaks, associated with the C–H stretching modes that shift to lower energies when hydrogen is substituted by deuterium. In contrast, other narrow peaks, associated with the H–H stretching vibration mode, are characteristic of the adsorbed molecular hydrogen. Therefore, Raman spectroscopy could be useful for the study of the hydrogen distribution in SWNT-H.

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The hydrogenation of SWNT reported by a number of research groups was performed at ambient conditions, as well as at elevated hydrogen pressure and liquid nitrogen temperature. For example, the hydrogenation of an impure SWNT sample performed at room temperature and 0.041 MPa results in a hydrogen storage density between 5 and 10 wt.% [1], while a storage density of ~ 4.2 wt.% has been reported at room temperature on purer samples for a hydrogen pressure of ~ 10 MPa [10]. Relatively pure SWNT were also hydrogenated at 80 K and 10 MPa hydrogen pressure, resulting in a storage density of ~ 8 wt.% [2]. The high-pressure/high temperature (HPHT) hydrogenation of SWNT was predicted theoretically to be very effective [3] and a recent work at a hydrogen pressure of 9 GPa and a temperature of 450 °C has resulted in thermally stable SWNT-H containing ~ 6.5 wt.% of hydrogen [4]. The infrared (IR) measurements on these samples have shown the existence of chemically bound hydrogen associated with C–H vibration bands which disappeared after partial annealing and hydrogen removal to residual content of 3 wt.% [4].

In the present work, we have investigated high purity SWNT-H, hydrogenated at $P \approx 5.0$ GPa and $T \approx 500$ °C, by means of micro-Raman spectroscopy. Our primary motivation was the characterization of SWNT-H, hydrogenated at high hydrogen pressure and temperature, in order to reveal the specific features related to the adsorbed molecular and/or covalently bonded hydrogen.

2. Experimental

The starting SWNT was synthesized by the arc discharge evaporation method in helium atmosphere at a pressure of 0.86 bar using a metallic Ni/Y catalyst. A purification method, based on the multistep oxidation in air followed by multistep reflux in HCl, resulted in a ~ 90 wt.% content of SWNT. The average diameter of the SWNT were 1.5 nm (1.4–1.6 nm) as it follows from the preparation method and the transmission electron microscopy (TEM) 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 [11]. The main impurities were graphite nanoparticles in the order of 2–4 μm , while the total content of metal impurities was $\sim 1.3\%$. The final product was annealed in vacuum at 600 °C for 5 h.

The hydrogenation of SWNT was performed by their treatment at high hydrogen pressure at elevated temperature. A mass of 60 mg from the SWNT material was placed in a high-pressure chamber and saturated with hydrogen obtained by thermal decomposition of AlH_3 . The sample was held under a hydrogen pressure of 5 GPa at 500 °C for 10 h. At the end of this procedure, the chamber was cooled down to room temperature and then the pressure was released. The obtained samples of SWNT-H contained up to 5.5 wt.% of hydrogen and were kept in a cold-welded

aluminum container. The samples demonstrate high thermal stability as the major hydrogen content is released only at $T \geq 500$ °C, in agreement with an earlier study [4]. The hydrogenation procedure followed in this work is described in more detail in [12], where it was applied for the hydrogenation of the C_{60} fullerene.

Raman spectra from small SWNT-H pieces with typical dimensions of 100 μm were recorded in the back-scattering geometry using a micro-Raman setup equipped with a triple monochromator (DILOR XY) and a liquid nitrogen cooled CCD detector system. The 488 nm and 514.5 nm line of an Ar^+ laser, as well as the 647.1 nm line of a Kr^+ laser, were used for excitation. For consistency, all Raman spectra presented in the figures of this work have been excited by the 488 nm line. The laser line was focused on the sample by means of a 100 \times objective with a spatial resolution of ~ 1 μm , while the beam intensity was varied in the range 0.04–0.5 mW.

3. Results and discussion

The Raman spectra of pristine and hydrogenated SWNT are illustrated in Fig. 1. Spectrum (a) corresponds to the pristine SWNT; its Raman features, narrow peaks and a very small intensity of the D-band at 1350 cm^{-1} , are typical for SWNT of high structural order. It is known that 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 [13]. The intense Raman G-band at a higher energy corresponds to the C–C stretching vibrations in tangential and axial directions of the SWNT that splits to G^- (tangential) and G^+ (axial) bands located at 1567 cm^{-1} and 1592 cm^{-1} , respectively. The shape of the G^- -band is sensitive to the electronic proper-

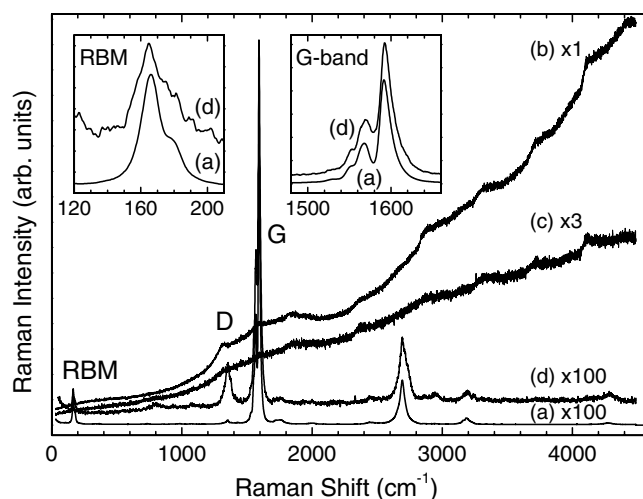


Fig. 1. Raman spectra of (a) pristine SWNT, (b) SWNT-H after annealing in vacuum at ~ 200 °C for 3 h, (c) at ~ 350 °C for 3 h and (d) at ~ 550 °C for 1 h. Insets: Raman spectra (a) and (d) in the RBM and the G-band frequency regions.

ties (strongly related to chirality) of SWNT: the Lorentzian lineshape is characteristic of semiconducting SWNT, whereas the Breit–Wigner Fano lineshape is typical for metallic SWNT [14]. In our case, the Lorentzian lineshape of the G^- -band (Fig. 1, inset) indicates that the probed SWNT are semiconducting. The low-frequency Raman band is related to the radial breathing modes (RBM) of the tubes and in our case it is comprised of a prominent peak located at 166 cm^{-1} and a high-energy shoulder near 178 cm^{-1} (Fig. 1, inset). The RBM frequency, ω_R , is inversely proportional to the tube diameter, d_t , while its value is upshifted owing to the intertube interaction within a SWNT bundle [14]. One of the empirical relations between d_t and ω_R , applicable for bundled SWNT is [14]:

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

According to Eq. (1), the main RBM peak at 166 cm^{-1} corresponds to SWNT with a diameter of $\sim 1.52\text{ nm}$, whereas the shoulder at 178 cm^{-1} is related to SWNT with a diameter of $\sim 1.41\text{ nm}$. These tube diameters are in good agreement with those estimated by the TEM observations.

Numerous weak features that appear in the Raman spectra of SWNT are related to the double-resonance one- and two-phonon processes, giving rise to combination modes and overtones, characteristic of the vibrational and electronic structure of the material [13,15,16]. Among them, the most interesting for our study are those with frequencies close to the Raman frequencies of the C–H stretching vibrations of the covalently bonded hydrogen ($2800\text{--}3000\text{ cm}^{-1}$) and of the H–H stretching vibration of molecular hydrogen ($4130\text{--}4160\text{ cm}^{-1}$). In these regions, a number of second-order Raman peaks appears, which are related to the 2D mode (2692 cm^{-1}), the $2G^-$ mode (3133 cm^{-1}), the $G^- + G^+$ mode (3160 cm^{-1}), the $2G^+$ mode (3186 cm^{-1}), the $2D + G^-$ mode (4259 cm^{-1}), and the $2D + G^+$ mode (4284 cm^{-1}).

The diffuse and structureless spectrum (b) in Fig. 1 refers to the hydrogenated SWNT. Its intensity is about a hundred times stronger than that of the pristine SWNT. The high intensity and the frequency dependence of this spectrum are typical characteristics of hot luminescence. This is further supported by the fact that the spectrum intensity and frequency dependence do not change if we alternatively use the 647.1 nm line of a Kr^+ laser for excitation (not shown). The high luminescence background screens the Raman features related to the pristine SWNT material. Note that, the spectrum (b) was recorded after sample annealing in vacuum at $200\text{ }^\circ\text{C}$ for 3 h and that the Raman spectrum of the as-prepared SWNT-H is even more intense. The intensity of the spectrum decreases after further vacuum annealing at $350\text{ }^\circ\text{C}$ for 3 h (spectrum (c) in Fig. 1), but the principal changes appear after vacuum annealing at $550\text{ }^\circ\text{C}$ for 1 h (spectrum (d) in Fig. 1). The latter annealing process results in a nearly zero luminescence background and spectrum (d) demonstrates the basic Raman features of the pristine SWNT, that is, the RBM modes, the split G-band, the D-band, and the weak sec-

ond-order Raman peaks. Note that, the more intense D-band and the peak broadening in spectrum (d) are indications of a relatively higher structural disorder of the annealed SWNT-H as compared to the pristine SWNT material. In addition, a new weak Raman peak appears in spectrum (d) at 2944 cm^{-1} that may be attributed to the C–H stretching mode of covalently bonded hydrogen as well as to the second-order $D + G^+$ combination mode.

Fig. 2 shows the Raman spectra of the SWNT-H annealed in air under various conditions. Spectrum (a) corresponds to the pristine SWNT, whereas spectra (b) and (c) refer to SWNT-H annealed in air at $\sim 330\text{ }^\circ\text{C}$ for 0.5 h and at $\sim 330\text{ }^\circ\text{C}$ for 1.5 h, respectively. Annealing in air is more effective than in vacuum as the luminescence background decreases more rapidly and at lower temperatures compared to the vacuum annealing. The spectra in Fig. 2 show a gradual decrease of the structural disorder in SWNT-H when the annealing time increases: the Raman peaks in spectrum (c) are narrower than in spectrum (b), resulting in an observable splitting of the G-band into G^- and G^+ components. In addition, the residual luminescence background and the intensity of the D-band decrease with increasing annealing time, whereas the low-energy RBM peak becomes more prominent (Fig. 2, inset). A gradual decrease of the luminescence background was also observed under laser irradiation of the as-prepared SWNT-H at high laser power densities and for long exposition times. This may be related to the sharp focusing of the laser beam that results in sample overheating. To prevent the laser overheating effect, we have used laser intensities as small as 0.04 mW for the Raman measurements on the as-prepared SWNT-H.

The occurrence of the luminescence background in SWNT-H might be attributed to the HPHT treatment effect on the pristine SWNT rather than to the hydrogen adsorption. To check this alternative, we have also mea-

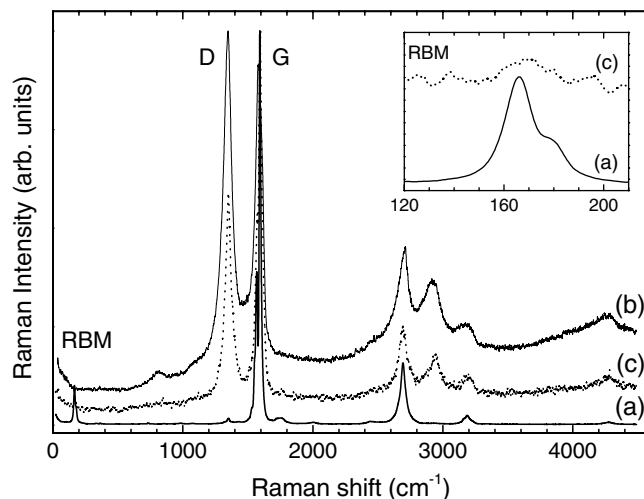


Fig. 2. Raman spectra of (a) pristine SWNT, (b) SWNT-H after annealing in air at $\sim 330\text{ }^\circ\text{C}$ for 0.5 h, and (c) at $\sim 330\text{ }^\circ\text{C}$ for 1.5 h. Inset: Raman spectra (a) and (c) in the RBM frequency region.

sured the Raman spectrum of SWNT treated under the same P , T conditions as those used for the SWNT-H preparation ($P = 5.0$ GPa, $T = 500$ °C) but without hydrogen atmosphere. The spectrum of thus treated SWNT is compared with the spectrum of the pristine SWNT in Fig. 3, spectra (b) and (a), respectively. Note that, the luminescence background in spectrum (b) of the HPHT treated SWNT is not as high as in the spectra of hydrogenated SWNT in Fig. 1, and that the main Raman features of the pristine SWNT remain almost the same. Close inspection of the RBM band in the HPHT treated material reveal that the relative intensity of the peak attributed to larger tubes decreases (Fig. 3, inset), denoting possibly the larger tube cross-section deformation under the pressure and temperature conditions used. Furthermore, the broadening of all the observed Raman peaks, the increase of the D-band intensity, the appearance of the second-order D + G⁺ peak at ~ 2945 cm⁻¹ and the background enhancement indicate the relatively high structural disorder of the material due to the HPHT treatment. Note that, these observations are consistent with an earlier study, where even the SWNT polymerization upon HPHT treatment has occurred at higher pressures than the one used here [17]. Vacuum annealing of the HPHT treated SWNT at 550 °C for 1 h does not change significantly the Raman features (spectrum (c) in Fig. 3). Thus, the high luminescence background in the Raman spectrum of SWNT-H, compared to that of the pristine material, should be regarded as the consequence of nanotube hydrogenation.

In search of Raman peaks attributed to covalently bonded hydrogen, we have investigated the isotopic effect on the C–H stretching vibrations by means of deuterium substitution of hydrogen. As mentioned above, in carbon-related materials the C–H stretching modes originating from covalently bonded hydrogen show intense

Raman peaks in the frequency region of 2800–3000 cm⁻¹, which should be downshifted upon deuterium substitution of hydrogen. Raman spectra were acquired from deuterated SWNT (SWNT-D) samples that were prepared by SWNT deuteration at 5 GPa and 500 °C for 10 h. These samples have been characterized by mass-spectroscopy and they have been found to contain ~ 10.5 wt.% deuterium [18], indicating that the atomic concentration of the light element is similar in deuterated and hydrogenated SWNT. The Raman spectrum of the as-prepared SWNT-D, like in the case of SWNT-H, demonstrates a giant luminescence background that decreases under air or vacuum annealing. Fig. 4 presents a comparison between the Raman spectrum of the pristine SWNT (spectrum (a)) with that after hydrogenation or deuteration followed by vacuum annealing at 550 °C for 1 h (spectra (b) and (c), respectively). The spectra (b) and (c) are nearly identical and their differences from that of the starting SWNT material are indicative of an increased structural disorder introduced by the hydrogen isotopes and the corresponding HPHT treatment. The coincidence of the peak positions in spectra (b) and (c) indicates that there is no isotopic shift related to deuterium substitution of hydrogen, suggesting that the observed peaks are not related to covalently bonded hydrogen. Consequently, the peak at ~ 2944 cm⁻¹ in the Raman spectrum of both SWNT-H and SWNT-D, should be assigned to the second-order D + G⁺ combination mode. On the basis of the above observations, it appears that the annealed SWNT-H and SWNT-D samples at 550 °C for 1 h do not contain any significant density of covalently bonded hydrogen. This finding is also consistent with the mass-spectroscopic data [18].

The Raman modes of molecular hydrogen are located in two spectral regions, 350–650 cm⁻¹ and 4100–4200 cm⁻¹, as it can be deduced by the reference Raman spectrum

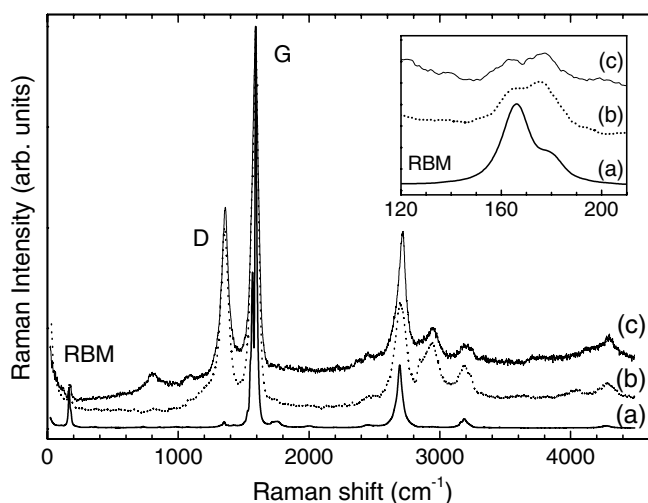


Fig. 3. Raman spectra of (a) pristine SWNT, (b) HPHT treated SWNT in the absence of a hydrogen atmosphere, and (c) HPHT treated SWNT after annealing in vacuum at ~ 550 °C for 1 h. Inset: Raman spectra (a–c) in the RBM frequency region.

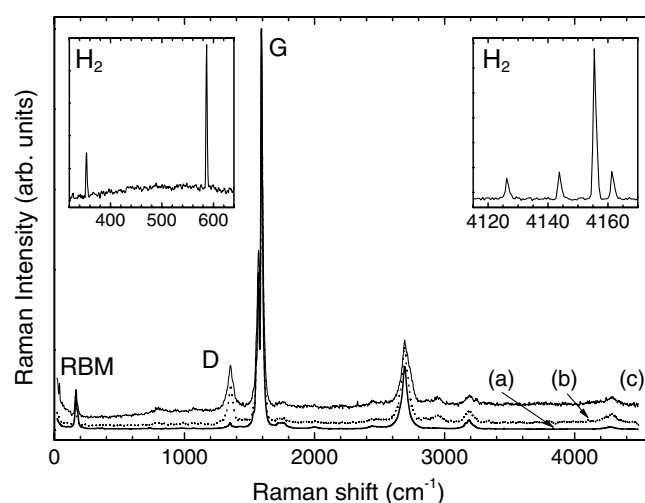


Fig. 4. Raman spectra of (a) pristine SWNT, (b) SWNT-H after annealing in vacuum at ~ 550 °C for 1 h, and (c) the SWNT-D after annealing in vacuum at ~ 550 °C for 1 h. Insets: Raman spectra of molecular hydrogen at 5 bar in two different spectral regions.

measured in a quartz vessel filled with pure molecular hydrogen at $P = 5$ bars. More specifically, the Raman spectrum of the molecular hydrogen, shown in the insets of Fig. 4, consists of six very sharp peaks at 353, 587, 4126, 4143, 4155, and 4161 cm^{-1} . On the contrary, the spectrum (b) of SWNT-H in Fig. 4 does not contain any sharp peaks in these frequency regions that can be attributed to H–H stretching vibrations but rather some weak and broad Raman features, related to the second-order $2D + G^-$ and $2D + G^+$ combination modes at 4259 cm^{-1} and 4284 cm^{-1} , respectively.

It is interesting to compare our Raman measurements with the IR spectra of the as-prepared SWNT-H that show distinct peaks in the range 2860–2920 cm^{-1} , related with the C–H stretching vibration modes [4]. These peaks demonstrate a large isotopic shift in SWNT-D due to deuterium substitution of hydrogen. The intensity of the C–H vibration peaks gradually decreases upon vacuum annealing, and the peaks disappear in the samples annealed in vacuum at 550 °C [4]. Therefore, it is most likely that the absence of the peaks at isotope-dependent energies in the present Raman spectra is connected with the vanishingly small hydrogen density in SWNT-H after annealing. The main characteristic of the Raman spectrum of the as-prepared SWNT-H is a giant background that masks the Raman peaks of the hydrogenated material, making the identification of the C–H and H–H stretching vibrations impossible. This background, associated with hot luminescence, should be attributed to a high structural disorder, mainly induced by the formation of the C–H covalent bonds with a random distribution over the tubules upon SWNT hydrogenation at high hydrogen pressure. The removal of bonded hydrogen from SWNT-H upon annealing restores the structural order of the starting SWNT material and results in the diminution of the luminescence background in the Raman spectra. The content of the covalently bonded hydrogen in the SWNT-H sample gradually decreases upon vacuum annealing and this process becomes very fast at 550 °C, in agreement with the IR measurements [4]. A similar decrease of the covalently bonded hydrogen content takes also place upon SWNT-H annealing in air even at lower temperatures, which could be attributed to hydrogen oxidation in ambient atmosphere.

Finally, it is important to note the similarity between the Raman spectra of the pristine SWNT and the annealed SWNT-H after the complete hydrogen release. This similarity suggests that the adsorbed or covalently bonded hydrogen does not cause significant damage to the structure of the starting SWNT material during the HPHT hydrogenation process. On the contrary, the HPHT treatment of SWNT without hydrogen atmosphere induces a considerable structural disorder of the nanotubes.

In conclusion, the Raman spectra of SWNT hydrogenated at high hydrogen pressure and elevated temperature are measured by means of micro-Raman spectroscopy. The Raman spectra of the as-prepared SWNT-H are very diffuse and structureless due to a large luminescence background that vanishes after sample annealing in vacuum or in air. The annealing of the SWNT-H sample outgasses both the chemically bonded and the adsorbed hydrogen and restores the structural ordering of the pristine SWNT material.

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