



Raman Study of Hydrogenated and Fluorinated Single-walled Carbon Nanotubes

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Abstract: Hydrogenated and fluorinated single-walled carbon nanotubes (SWNT-H and SWNT-F) were investigated by micro-Raman spectroscopy. The as-prepared SWNT-H exhibits giant structureless hot luminescence that screens the Raman peaks. The luminescence background, attributed to random binding of the hydrogen atoms, gradually decreases upon annealing of the sample. In contrast, the as-prepared SWNT-F shows no luminescence but the Raman peaks are rather broad. The annealing of SWNT-F results in structural ordering due to fluorine removal.

Keywords: Single-walled carbon nanotubes, Raman spectra, Hydrogenation, fluorination

Single-walled carbon nanotubes can be used for hydrogen storage as the molecular hydrogen can fill the interior of the nanotubes or the space between them within a bundle (1). Hydrogen can also form C-H bonds with the carbon atoms of SWNT or the fullerene C₆₀ (2). Similar bonds between carbon and fluorine atoms can be formed upon fluorination of SWNT (3). In this work, we compared the Raman spectra of SWNT-H

and SWNT-F with that of the initial SWNT to reveal the changes induced by the addition of hydrogen or fluorine, as well as by their removal upon material annealing.

The SWNT used for hydrogenation were synthesized by the arc-discharge evaporation method in helium atmosphere at a pressure of 0.86 bar using a metallic Ni/Y catalyst. No surfactants were used during the purification procedure. The multistep oxidation in air followed by multistep reflux in HCl, resulted in a ~ 90 wt% content of SWNT. The main impurities were graphite particles with diameter $\leq 4 \mu\text{m}$, while the total content of metal impurities was $\sim 1.3\%$. The final product was annealed at 600 °C in vacuum for 5 hours. The average diameter of the SWNT sample was 1.5 nm, as determined from Raman and TEM characterization. The hydrogenation of SWNT performed by high temperature treatment at high hydrogen pressure resulted in 5.5 wt% uptake of hydrogen (4). 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 SWNT used for fluorination was synthesized by the HiPCO process. The purification from residual iron catalyst and nontubular forms of carbon involved the oxidation of raw SWNT material at 250 °C for 22 hours by wet O_2 , followed by 4 hours sonication in HCl. The material was then washed, dried and annealed in Ar at 800 °C for 1 hour to remove the functional groups introduced by oxidation. By repeating this procedure for three times, the metal content was reduced to ~ 0.6 at .wt% Fe. Raman spectroscopy and AFM characterization yield nanotube diameters and lengths in the ranges of 0.8–1.3 nm and 0.8–3 μm , respectively. The purified SWNT sample was fluorinated in a custom-built fluorination apparatus for 2–4 hours at 150 °C. The bulk stoichiometry of the SWNT-F samples was approximately C_5F_2 , according to the weight gain and the SEM/EDX elemental analysis.

Raman spectra from small SWNT-H and SWNT-F pieces with typical dimensions of 100 μm were recorded in the back-scattering geometry using a micro-Raman setup composed of a triple monochromator DILOR XY and a CCD detector system, cooled at liquid nitrogen temperature. 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, while the beam intensity on the sample was varied in the range 0.04–0.5 mW. The laser beam was focused on the sample by means of a 100 $\times$ objective with a spatial resolution of $\sim 1 \mu\text{m}$.

The Raman spectra of pristine and hydrogenated SWNT are shown in Figure 1. The spectrum in Figure 1(a) corresponds to the pristine SWNT; the narrow peaks and the small intensity of the disorder-induced D-band at 1350 cm^{-1} are typical for SWNT of high structural order (5). The intense band corresponds to the tangential C-C stretching vibrations

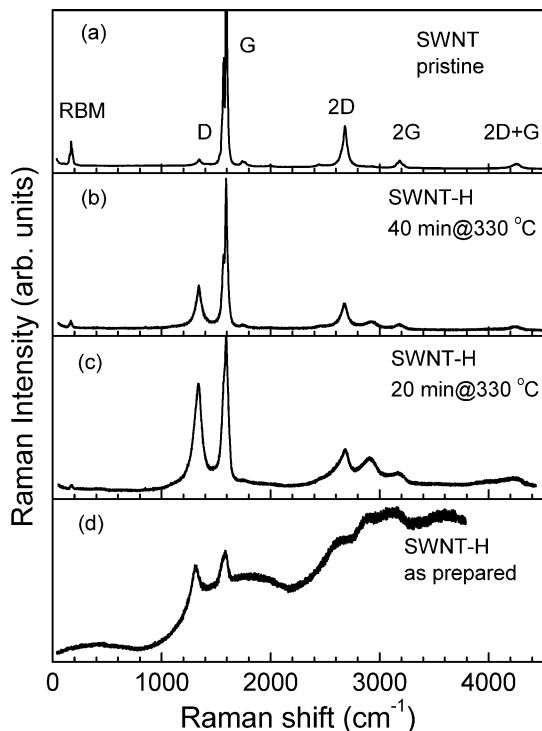


Figure 1. Ambient conditions Raman spectra of (a) the pristine arc-discharge SWNT and (b)–(d) the SWNT-H material before and after annealing at 330°C.

that split to components corresponding to vibrations perpendicular (G^-) and parallel (G^+) to the tube axis, located at 1567 cm^{-1} and 1592 cm^{-1} , respectively. The Lorentzian lineshape of the G^- -band in our case is characteristic of semiconducting SWNTs (6). The low-frequency Raman band, related to the radial breathing modes (RBM), comprising a prominent peak at 166 cm^{-1} and a high-energy shoulder near 178 cm^{-1} . According to the empirical relations between the RBM frequency and the tube diameter, these peaks correspond to SWNT with diameters of ~ 1.52 and $\sim 1.41\text{ nm}$, respectively (6).

Numerous other features in the Raman spectra of SWNT are related to double-resonance one- and two-phonon processes, giving rise to combination modes and overtones (5). Among them, the most interesting for our study are those with frequencies close to the Raman frequencies of the C-H stretching vibrations of 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 appear, which are related to the 2D mode (2692 cm^{-1}), the 2G modes ($3133\text{--}3186\text{ cm}^{-1}$) and the 2D+G modes ($4259\text{--}4284\text{ cm}^{-1}$).

The diffuse spectrum in Figure 1(d) that consists of weak Raman peaks and intense luminescence background corresponds to the as-prepared hydrogenated SWNT. The frequency dependence and the high intensity of the luminescence background are typical for hot luminescence. The background drastically decreases after annealing in air at 330°C for 20 minutes (Figure 1c). The additional annealing results in a nearly zero luminescence background and the spectrum demonstrates the RBM modes, the split G-band, the D-band, and the weak second-order Raman peaks (Figure 1b). The decrease of the D-band intensity and the peak narrowing are indications of structural ordering. Nevertheless, the annealed SWNT-H remains less ordered as compared to the pristine SWNT material. A weak peak at 2944 cm^{-1} appearing in the spectra of annealed SWNT-H could be attributed to the C-H stretching mode of covalently bonded hydrogen or to the second-order D+G combination mode. To verify this possibility, we have investigated the isotopic effect by means of deuterium substitution of hydrogen that should shift down the C-H stretching vibration frequencies. The Raman spectra were acquired from deuterated SWNT samples (SWNT-D) that have been found to contain $\sim 10.5\text{ wt\%}$ deuterium, indicating similar atomic concentration to hydrogen in SWNT-H. The Raman spectrum of the as-prepared SWNT-D demonstrates also a giant luminescence background that decreases under sample annealing in air. Figure 2 presents a comparison between the Raman spectra of the as-prepared SWNT-D (Figure 2a) with those of the SWNT-D annealed in air at 330°C for 20 minutes (Figure 2b) and of the SWNT-H annealed in air at 330°C for 40 minutes (Figure 2c). In spectra (b) and (c), the same frequencies of the peaks that may be attributed to the C-H stretching modes (marked by the arrows in the figure) indicate that there is no isotopic shift related to deuterium substitution of hydrogen. Consequently, the peak at $\sim 2944\text{ cm}^{-1}$ in the Raman spectrum of both SWNT-H and SWNT-D should be assigned to the second-order D+G combination mode.

It is interesting to compare the phonon spectra of hydrogenated with those of fluorinated SWNT. The Raman spectrum of the pristine HiPCO SWNT (Figure 1a) differs from that of the arc-discharge SWNT in the RBM and G-band regions due to the different tube diameter distributions (Figure 3a). The narrow peak lineshapes and the weak D-band around 1350 cm^{-1} indicate a relatively high structural order of the initial HiPCO SWNT. On the other hand, the Raman spectrum of SWNT-F displays a weaker RBM, a broad G- and an intense D-band, whereas the luminescence background is rather small (Figure 3b). It is interesting to note that the peak related to the C-F stretching vibration at $\sim 1120\text{ cm}^{-1}$ is very weak, and the main effect of fluorination is the broadening of Raman peaks and the enhancement of the D-band. These effects are indications of an increased structural disorder of SWNT upon

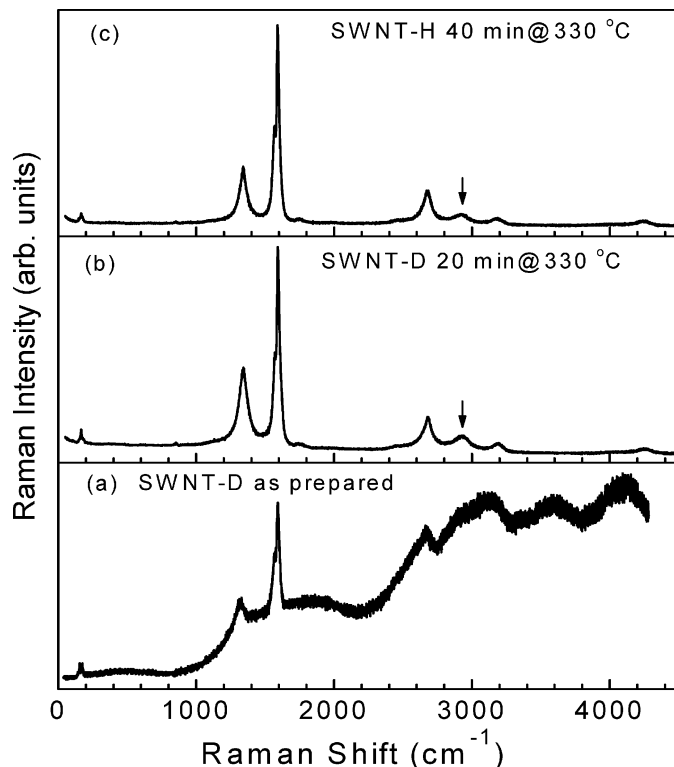


Figure 2. Ambient conditions Raman spectrum of (a) the as-prepared SWNT-D and (b) after 20 minutes annealing at 330°C (c) the SWNT-H after 40 minutes annealing at 330°C.

fluorination. The structural disorder manifested in the Raman spectra of SWNT-F is most likely related to the random creation of C-F covalent bonds that distort the translational symmetry in the nanotubes. The intensity of the D-band decreases considerably after annealing at 345°C of SWNT-F in air. This is accompanied by the reduction of the G-band width (inset in Figure 3). This behavior is consistent with earlier published data that reveal almost complete fluorine removal after annealing of SWNT-F at $T > 300^\circ\text{C}$ (7). However, the remaining D-band intensity is considerably higher than that in the initial SWNT, indicating residual structural disorder, which is most likely induced by another type of defect created during the sample annealing.

The infrared spectra of the as-prepared SWNT-H show distinct C-H stretching vibration peaks in the range $2860\text{--}2920\text{ cm}^{-1}$, which demonstrate a large isotopic shift in SWNT-D due to deuterium substitution of hydrogen (4). The intensity of the C-H vibration peaks gradually decreases upon

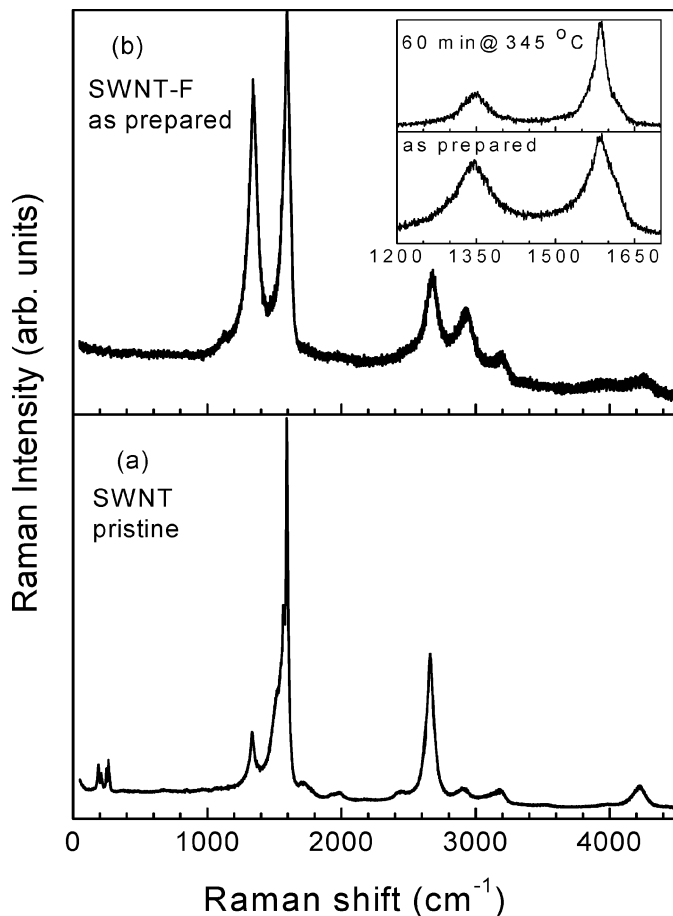


Figure 3. Ambient conditions Raman spectrum of (a) the pristine HiPCO SWNT and (b) the as-prepared SWNT-F. Inset illustrates the Raman spectra in the frequency region of the D- and the G-bands for the as-prepared SWNT-F and after 60 minutes annealing at 345°C.

annealing, and the peaks disappear in samples annealed at 550°C in vacuum (4). On the contrary, the Raman spectra of the as-prepared SWNT-H show a giant luminescence background that masks the Raman features of the hydrogenated material. This background, associated with hot luminescence, reflects a structural disorder, mainly induced by the formation of C-H covalent bonds upon SWNT hydrogenation with a random distribution over the tubules. 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 SWNT-H

gradually decreases upon annealing, and this could be the reason for the absence of C-H stretching vibration modes in the Raman spectra of the annealed samples. On the other hand, the Raman spectra of fluorinated SWNT are free of luminescence background. Nevertheless, the intensity of the C-F stretching vibration peak is very small despite the high content of bonded fluorine. Both hydrogenated and fluorinated SWNT show high structural disorder related to a random covalent bonding of hydrogen and fluorine, which distorts the translational symmetry of nanotubes. This could also explain the absence or the low signal of the C-H and the C-F stretching vibration modes, as the distorted translational symmetry reduces the coherence of these vibrations and their intensity in the Raman spectra drops down.

Finally, it is important to note the similarity between the Raman spectra of the pristine SWNT and the annealed SWNT-H and SWNT-F after their complete outgassing, which suggests that the functionalization does not damage the structure of the SWNT.

ACKNOWLEDGMENTS

The support by the Russian Foundation for Basic Research, grant No 08-02-00890, and the support of the General Secretariat for Research and Technology (Greece) and Russian Academy of Sciences under the bilateral Greek-Russian collaboration program, are greatly acknowledged.

REFERENCES

1. Frankland, S.J.V., and Brenner, D.W. (2001) Hydrogen Raman shifts in carbon nanotubes from molecular dynamics calculation. *Chem. Phys. Lett.*, 334: 18–23.
2. Bini, R., Ebenhoch, J., Fanti, M., Fowler, P.W., Leach, S., Orlandi, G., R  chardt, Ch., Sandall, J.P.B., and Zerbetto, F. (1998) The vibrational spectroscopy of C₆₀H₃₆: An experimental and theoretical study. *Chem. Phys.*, 232: 75–94.
3. Mickelson, E.T., Huffman, C.B., Rinzler, A.G., Smalley, R.E., Hauge, R.H., and Margrave, J.L. (1998) Fluorination of single-wall carbon nanotubes. *Chem. Phys. Lett.*, 296: 188–194.
4. Bashkin, I.O., Antonov, V.E., Bazhenov, A.V., Bdikin, I.K., Borisenko, D.N., Krinichnaya, E.P., Moravskii, A.P., Kharkunov, A.I., Shul'ga, Yu. M., Ossipyan, Yu. A., and Ponyatovskii, E.G. (2004) Thermally stable hydrogen compounds obtained under high pressure on the basis of carbon nanotubes and nanofibers. *JETP Lett.*, 79: 226–230.
5. Thomsen, C., and Reich, S. (2000) Double resonant Raman scattering in graphite. *Phys. Rev. Lett.*, 85: 5214–5217.

6. Venkateswaran, U.D. (2004) Squeezing carbon nanotubes. *Phys. Stat. Sol. (b)*, 241: 3345–3351.
7. Pehrsson, P.E., Zhao, W., Baldwin, J.W., Song, G., Liu, J., Kooi, S., and Zheng, B. (2003) Thermal fluorination and annealing of single-wall carbon nanotubes. *J. Phys. Chem.*, 107: 5690–5695.