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Micro-Raman scattering of selenium-filled double-walled carbon nanotubes: Temperature study

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Selenium-filled double-walled carbon nanotubes (Se@DWNT) have been studied by high resolution transmission electron microscopy (HRTEM) and micro-Raman spectroscopy in the temperature interval from 80 to 600 K employing 785 nm excitation wavelength. The temperature dependences of the dominant bands (*G*-band and *G'*-band) are analyzed in terms of the model developed by Klemens [Phys. Rev. **148**, 845 (1966)], Hart *et al.* [Phys. Rev. B **1**, 638 (1970)], Cowley [J. Phys. (France) **26**, 659 (1965)] and extended by Balkanski *et al.* [Phys. Rev. B **26**, 1928 (1983)] for anharmonic decay of optical phonons. The findings were compared to analogous study for empty double-walled carbon nanotubes (DWNTs). The DWNT interatomic force constant modification as a result of the presence of the Se atoms inside the tubes is revealed through larger anharmonicity constants describing the temperature dependences of the *G'*-band and the inner tube tangential modes (*G*-band)

INTRODUCTION

The synthesis of monodimensional nanocrystals is complex due to the lack of stability of such structures. One way to stabilize them is to prepare them within a container, such as a carbon nanotubes (CNTs) due to their inner diameter in the nanometer range, as well as their good chemical and thermal stabilities. Selenium, which is a *p*-type semiconductor, exhibits both photovoltaic and photoconductive properties. It is utilized in many devices ranging from solar cells to rectifiers and xerography.¹ The aim of this work is to use Raman spectroscopy to investigate how the presence of Se inside double-walled CNTs (DWNTs) can modify their electronic properties. Selenium displays various crystallographic structures depending on the temperature and pressure conditions. Trigonal selenium (hexagonal) is the most stable allotrope under normal temperature and pressure. Selenium has also monoclinic allotropes² although it is generally commercially available in the amorphous state. The confinement of Se inside CNT was only scarcely studied, but Chancolon *et al.*³ proposed a method for filling CNT in the vapor phase and performed a comprehensive study of the structure of Se within the CNT by x-ray diffraction and x-ray absorption spectroscopy. They found that the Se present inside the CNT was mainly amorphous in their synthesis conditions. Earlier studies have revealed that the space available within CNT may play an important role on the crystal structure of the confined material, especially in the case of narrow DWNT where materials are often found in amorphous state even if they crystallize in single-walled CNT (SWCNT) of similar inner diameter.⁴ A recent study by Rodrigues *et al.*⁵ described the possibility to decorate bundles of SWCNT with a trigonal Se shell using an organolithium synthesis route, but no filling of the SWCNT was reported using this technique.

In this work we report the filling of DWNT by selenium using a capillary effect technique with melted Se and their characterization by micro-Raman spectroscopy in the temperature range between 80 and 600 K.

EXPERIMENTAL

DWCNTs were prepared as described in earlier work⁶ by catalytic chemical vapor deposition by decomposition of a H₂–CH₄ mixture over a MgO-based catalyst. DWNTs were filled using a capillary technique.^{7–9} 10 mg DWNT was mixed and gently ground together with 65 mg of gray (hexagonal) Se powder (99.999% purity, Aldrich). The mixture was vacuum sealed in a quartz ampoule which was heated in a programmable furnace at 5 K min^{−1} to 573 K (i.e., clearly above the melting point of Se which is 494 K) followed by a dwell at this temperature for 24 h followed by cooling to 373 K at 0.1 K min^{−1} and then down to room temperature at 1 K min^{−1}. Elimination of extraneous material deposited outside the CNT was investigated.¹⁰ Se can only be removed by concentrated acid treatment. Concentrated nitric acid (52.5 wt %), hydrochloric acid (37 wt %) and sulfuric acid (95 wt %) were investigated at room temperature and only concentrated nitric acid was able to dissolve Se in the form we used (hexagonal, as determined by x-ray powder diffraction analysis). Because the dissolution with nitric acid is performed at room temperature, we do not expect any damaging of the DWNT during the cleaning procedure.

Raman spectra were acquired using a Leica DMLP microscope coupled to a Raman system manufactured by Kaiser Optical Systems Inc. The RamanRxnTM analyzer incorporates the TE-cooled charge-coupled device detector for maximum sensitivity, InvictusTM NIR semiconductor laser with wavelength of 785 nm (1.58 eV), and holographic grating to provide fast, simultaneous full spectral collection of Raman data. The spectral resolution of this Raman system is

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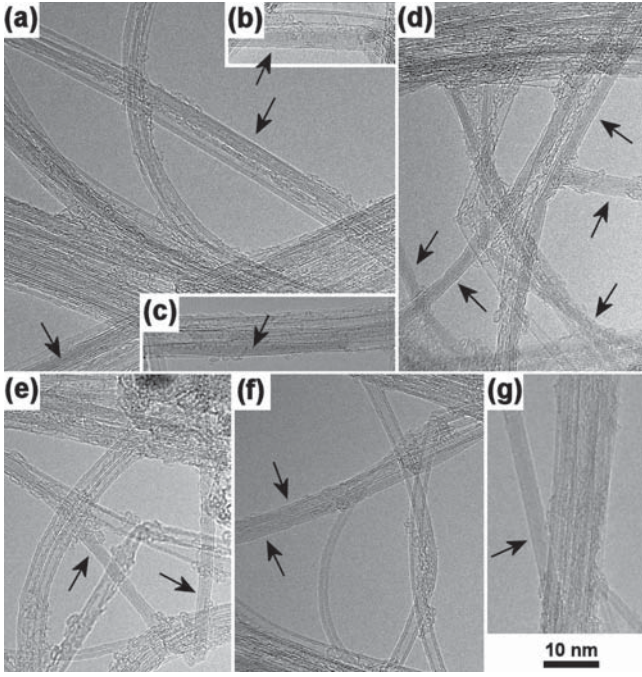


FIG. 1. HRTEM images of Se@CNT. Both SWCNT [(d) and (e)] and DWCNT [(b) and (g)] are filled. When CNT overlap [(a), (c), and (f)], the number of walls cannot be determined.

about 5 cm^{-1} . The laser spot diameter on the sample was $50 \text{ }\mu\text{m}$. The power density was maintained at the lowest level possible at this setup of $2 \text{ }\mu\text{W}/\mu\text{m}^2$. Heating effects from the laser irradiation are negligible at this power density level.¹¹ The samples were heated in a Linkam THMS 600 heating stage in static air from 80 to 600 K. At each data point, 40 K apart, the sample was left to thermalize for 15 min. Extreme care was taken to assure identical position of the laser spot at each temperature point. All spectra were normalized to the peak intensity of the strongest band in the spectra, namely, the *G*-band. All the numerical manipulations of the spectra were performed with GRAMS/AL 7.02 (Thermo Electron Corporation) and ORIGINPRO (Origin Lab Corporation) software.

RESULTS AND DISCUSSION

Figure 1 shows representative images of the Se-filled DWNT obtained by high-resolution transmission electron microscopy (HRTEM). From HRTEM observation we can estimate that the filling yield is probably between 40% and 50%. Some coating can be observed on the CNTs, which could correspond either to amorphous carbon or to Se. Black arrows indicate Se-filled CNT. The filling appears to be exclusively amorphous, as opposed to the hexagonal phase used as starting material. This could be due to the small space available within the DWNT (Ref. 10) but is most likely due to the fact that no crystalline phase could be stabilized in the experimental conditions used. Energy dispersive x-ray (EDX) analysis of either isolated filled DWNT or bundles confirmed the presence of Se.

G-band (TM-band in some references) is the most intense Raman spectral feature $1550\text{--}1600 \text{ cm}^{-1}$. It is a result of tangential C–C bond stretching. Symmetry assignments of

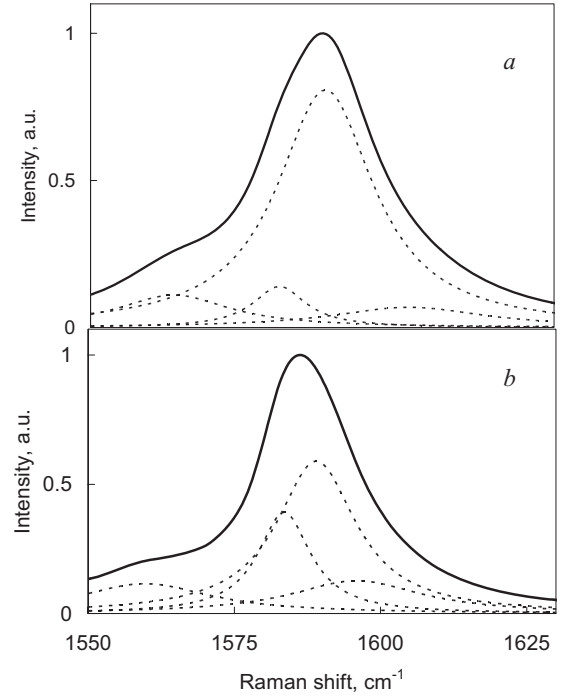


FIG. 2. *G*-band of Se@DWCNT (a) pristine and DWCNT (b) at 296 K fitted by four Lorentzian line shapes.

four Lorentzian components of the *G*-band [$\sim 1549(\omega_{E_2^-})$, $\sim 1567(\omega_{G^-})$, $\sim 1590(\omega_{G^+})$, and $\sim 1607(\omega_{E_2^+})$] cm^{-1} of single semiconducting SWCNT have been reported.¹² It has been established that the *G*-band of the metallic SWCNT consists of two components: a Lorentzian line shape higher frequency component at around 1580 cm^{-1} and a Breit–Wigner–Fano line shape component at lower frequencies $\sim 1545 \text{ cm}^{-1}$.¹³ Since the samples we studied were composed of tubes with a large size distribution,⁶ with diameters ranging from 0.5 to 3 nm and the energy of the excitation photons, 1.58 eV, matches the E_{11}^S , E_{22}^S , E_{11}^M (in the order of increasing tube diameter) electronic transitions for SWCNTs, obtained from tight-binding calculations,¹⁴ theoretically one should expect at least six components in the *G*-band. However, for comparative reasons, we analyzed the *G*-band of the DWCNT powder samples by fitting it with the minimum number of Lorentzian line shapes, in this case four, in the range from 1550 to 1635 cm^{-1} . The two lower frequency Lorentzians (*L1* and *L2*) represent the unresolved tangential modes in the strongly curved inner tubes (1563 and 1583 cm^{-1}) and two higher frequency Lorentzians (*L3* and *L4*) represent the unresolved tangential modes of the outer tubes (1591 and 1602 cm^{-1}), Fig. 2(a). This consideration is in agreement with published studies by other researchers.^{11,15} The uncertainty from the fitting procedure in determining the peak position of every component from the fit is not more than 1 cm^{-1} . The integral intensity of the dominant component (*L3*) at 1591 cm^{-1} ($\Gamma=20 \text{ cm}^{-1}$) is 55% of the integral intensity of the *G*-band compared to 6% contribution of the component *L2*, at 1583 cm^{-1} ($\Gamma=10 \text{ cm}^{-1}$). The lowest (*L1*) and the highest frequency (*L4*) components are weak and considerably broader. Figure 2(b) shows the resolved *G*-band of pristine DWNTs. One can easily notice that the relative

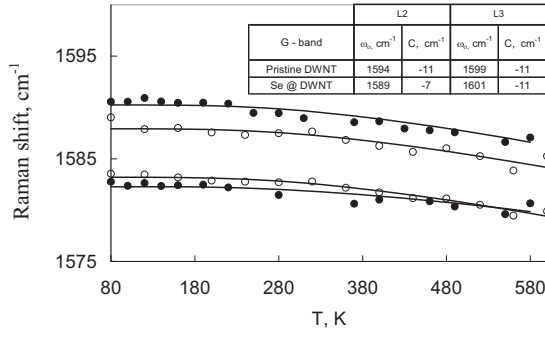


FIG. 3. Temperature dependence of L2 and L3 components of the G-band of pristine DWCNT (empty symbols) and Se@DWCNT (filled symbols).

integral intensity of L2 (1584 cm⁻¹, $\Gamma=11$ cm⁻¹) is 23%, while the dominant component at 1588 cm⁻¹ ($\Gamma=17$ cm⁻¹) has relative integral intensity of 49%. From comparing the resolved G-band in Figs. 2(a) and 2(b), we noticed considerable reduction in the relative integral intensity of the L2 component in the filled DWNT samples. Considering that the G-band L2 component is associated with the tangential modes of the inner carbon tubes, we can infer that this fact might be a direct evidence of the presence of the acceptor-type Se atoms affecting the electronic band structure of the inner tubes. One possibility might be that the inner tube of filled DWCNTs which have been in resonance with the excitation photons in the pristine DWCNT are not in resonance once the Se atoms were introduced as a result of charge transfer between the Se and the nanotubes surrounding them. From the fit it can be concluded that the dominant G-band component (L3) (the one which position is determined with minimum uncertainty) is consistently upshifted by small amount (around 3 cm⁻¹) as a result of the Se atoms inside the tubes. Similar blueshift of the G band (1064 nm excitation line) was reported recently for SWCNT intercalated by electron acceptors (S, Se, Te).¹⁶ The parameters acquired from the 80 K G-band fit are used as initial parameters for all G-band fitting procedures applied for each sample in their temperature study experiment. Thus obtained positions of the two middle components (L2 and L3) as a function of temperature are plotted in Fig. 3.

The temperature dependences of the frequency shift $\Omega(T)$ of the L2 and L3 components of the G-band, as well as the G'-band, are analyzed in terms of the model developed by Klemens,¹⁷ Hart *et al.*,¹⁸ and Cowley¹⁹ and extended by Balkanski²⁰ for anharmonic decay of optical phonons. The dominant optical mode frequencies of the G band and the second order G' band approximately corresponds to Debye temperatures of 2280 and 1850 K respectively. Consequently, the occupation number for the equivalent harmonic oscillator is less than 1 for the temperature range of our investigation (80–600 K). Therefore, our considerations are always in the quantum mechanical limit of a classical harmonic oscillator. Also shown in Fig. 3 are the numerical fits to the data (solid curve) specified by the expression reflecting the contributions of the three-phonon processes (cubic anharmonicity)²⁰ to the frequency shift,

$$\Omega(T) = \omega_0 + C \left[1 + \frac{2}{e^x - 1} \right], \quad (1)$$

where $x = \hbar\omega_0/2k_B T$ if simple Klemens¹⁷ approximation is applied, k_B is the Boltzman constant, ω_0 is a fitting parameter corresponding to the phonon frequency, and C is a fitting parameter corresponding to the contributions of the cubic anharmonicity to the phonon decay. The values for ω_0 and C for the filled and the pristine DWNT are listed in a table inserted in Fig. 3. Their uncertainty is not more than one unit in the last significant figure reported in this study. Comparing the anharmonicity constants, it is interesting to note that only the L2 component of the Se@DWNT has significantly changed its C value after the filling material is introduced. The latter can be attributed to stronger effects on the force constants associated with the tangential modes of the inner tubes when compared to those of the outer tubes. The smaller L2 anharmonicity constant concurs with the conclusion we drew above, namely, that after filling with Se our excitation photons are in resonance with a smaller subset of the DWNTs.

The G'-band (2D-band in some references) is due to two-phonon (second order) Raman scattering processes.²¹ The Raman D-band of the CNTs is a result of scattering in the presence of in-plane defects lowering the symmetry of the crystalline lattice. Its overtone, the G'-band is an intrinsic property of any sp^2 carbon material. Therefore, it is not selective to the CNT diameter (as the G-band), and it is much more intense than the disorder-induced D-band and is observed even when the D-band is absent (in crystalline graphite). The G' band can be fitted with a single Lorentzian line shape in the range from 2450 to 2700 cm⁻¹. G' band of Se@DWCNT is at 2583 cm⁻¹, which value is higher from that of the pristine DWNT by 4 cm⁻¹. This is in agreement with previously reported upshift of the G' band in Te@DWNT²² and PbI₂@DWCNT.²³ Figure 4 presents the position of the G'-band as a function of temperature. Also shown in Fig. 4 are the numerical fits to the data (solid curve) specified by the expression reflecting the contributions of the three-phonon (cubic anharmonicity) and four-phonon processes (quartic anharmonicity) to the frequency shift²⁰ applied to the second order band,

$$\Omega(T) = 2\omega_0 + 2C \left[1 + \frac{2}{e^x - 1} \right] + 2D \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right], \quad (2)$$

where x , ω_0 , and C are explained above, $y = \hbar\omega_0/3k_B T$, if simple Klemens¹⁷ approximation for a quartic anharmonicity, and D is a third fitting parameter corresponding to the contribution of the quartic anharmonicity to the phonon decay. In the above expression, ω_0 , C , and D can be associated with either one of the two identical optical phonons contributing to the second order G' band. The values of the three fitting parameters for each curve are listed in a table inserted in Fig. 4(a). The uncertainty in the fitting parameters is not more than a couple of units in the last significant figure. Anharmonicity contributions to the temperature shift of the G' band of

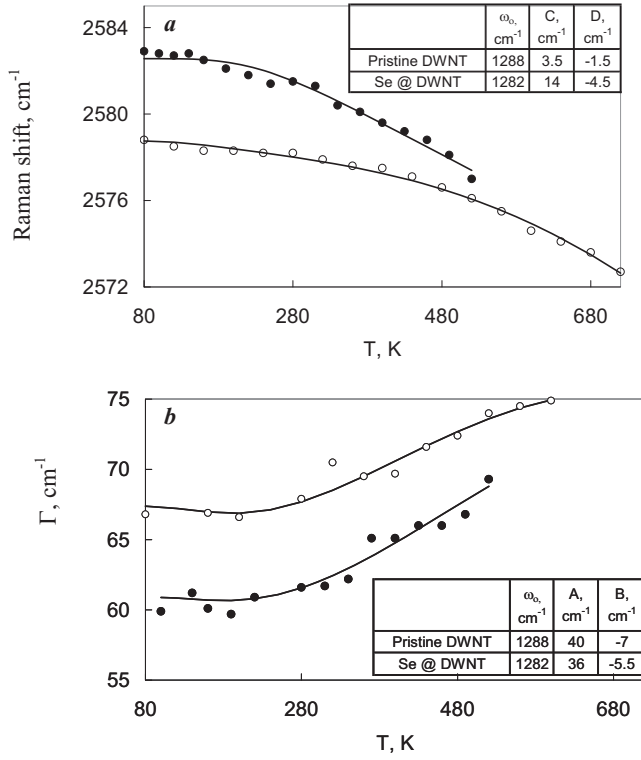


FIG. 4. Temperature dependence the G' -band position (a) and FWHM (b) of pristine DWCNT (empty symbols) and Se@DWCNT (filled symbols).

the Se@DWCNT is significantly larger than those of the pristine DWCNT. Therefore, we can conclude that Se atoms inside the CNTs enhance the anharmonic decay of the CNT phonons. Moreover, the presence of such effect is more convincing when it is exhibited in a band which is not nanotube diameter sensitive. Theoretical studies based on unsymmetrized self-consistent approximation, by Rabelo *et al.*²⁴ show that in addition to the nearest neighbors, the nonnearest neighbors give significant contribution to the crystal's surface atomic properties such as lattice relaxation and dynamics, which are relevant to the optical phonons of the DWNTs. Therefore, the additional interactions (force constants and charge transfer) due to the Se atoms incorporated in the inner tube space inevitably have changed the phonon characteristics of the DWNTs. In general, the absolute value of the ratio D/C is less than 1, in agreement with the expectation that the four-phonon processes have less contribution compared to the three-phonon processes.

The temperature dependence of the full width at half maximum (FWHM) of the G' band is shown in Fig. 4(b). The FWHM of the G' band, Γ , for each temperature point was found by fitting the band (1500–1660 cm⁻¹) with a single Lorentzian line shape. Also shown in Fig. 4(b) is the theoretical fit (solid curve), $\Gamma(T)$, specified by the expression²⁰

$$\Gamma(T) = 2A \left[1 + \frac{2}{e^x - 1} \right] + 2B \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right], \quad (3)$$

where x and y have the meaning as in expression (2) and A and B are the fitting parameters reflecting the anharmonicity

contributions. A and B can be associated with the decay rate of the two identical optical phonons contributing to the G' band. Their values are compared in a table inserted in Fig. 4(b). In order to decrease the uncertainty in the fitting parameters, the phonon frequency ω_0 was fixed to the value obtained from the fit of the temperature dependence of the frequency shift, $\Omega(T)$. By comparing A and B for the filled and pristine DWNTs, we see that the anharmonicity constants are not significantly different. Therefore $\Gamma(T)$ of the G' -band cannot be used conclusively for characterization of Se@DWCNT samples with large size distribution.

CONCLUSION

Systematic comparative experimental study (80–600 K) of the most prominent Raman bands of Se@DWCNT in powder form was carried out. G -band temperature shift is satisfactory described with cubic anharmonicity constant only. The decrease in the integral intensity and the decrease in the cubic anharmonic constant of the $L2$ component of the G -band associated with the inner tubes is attributed to the modified electronic transitions of the DWNTs due to the presence of the acceptor-type Se atoms. The G' -band temperature dependence can be fitted only if in addition to the cubic anharmonicity, a quartic anharmonicity is included. The anharmonicity constants for the Se@DWCNT are significantly larger than those of pristine DWNT due to the DWNT interatomic force constant modification as a result of the presence of the Se atoms inside the tubes. Therefore, the G' -band being nonselective to the tube diameter might be a sensitive probe for studying filled DWNTs.

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