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Research Article

Temperature Dependence of G^- Mode in Raman Spectra of Metallic Single-Walled Carbon Nanotubes

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The temperature evolution of G mode in the Raman spectra of surface grown single-walled carbon nanotubes (SWNTs) is investigated. It is revealed that the intensity of G^- mode in Raman spectra varies with the measurement temperature. The intensity variation of the G^- mode is synchronized to that of the radial breathing mode, which is sensitive to the resonance condition ($|E_L - E_{ii}|$). Such an intensity evolution is associated with the temperature-induced change of E_{ii}. That is, the intensity of G^-, an indication of electron-phonon coupling in metallic SWNTs, can be greatly enhanced only when the laser energy well matches the transition energy of nanotubes (E_{ii}). In other words, the window for observing asymmetric and broad G^- mode is very narrow. This work further confirms that the G^- mode in the Raman spectrum mainly arises from metallic SWNTs, and caution should be paid when using the intensity ratio of G^-/G^+ to estimate the percentage of metallic SWNTs in products.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have been the subject of intensive research because of their fascinating optical, electronic, and chemical properties [1–4]. An SWNT exhibits either metallic or semiconducting characteristics depending on its chiral indices (n, m) [3]. SWNTs with different conductivities function differently when they are incorporated into nanodevices [5, 6]. For example, semiconducting SWNTs can be the core component in field effect transistors [5] and metallic SWNTs may be well applied in highly conductive transparent thin films [6]. However, most produced SWNTs consist of both semiconducting and metallic species [7, 8]. To facilitate the separation and practical application of the metallic SWNTs, it is necessary to characterize them based on their intrinsic electrical properties. Among different optical characterization techniques, Raman spectroscopy is particularly sensitive to metallic SWNTs and is a facile technique to analyze as-produced SWNTs. The sensitivity to metallic species is partly due to the possible emergence of a broad, softened G^- peak, sometimes referred as a Breit-Wigner-Fano (BWF) line shape [9] in the Raman spectrum, which can unambiguously identify as a metallic nanotube [10–13]. Furthermore, the intensity/area ratio of the G^+ to the G^- band has been widely adopted to evaluate the relative concentration of semiconducting and metallic SWNTs in bulk products [14–16].

The G^- peak is the longitudinal mode of the metallic tube, and its broadening arises from coupling between the phonon and the electronic excitations, as predicated by theoretical calculations and verified experimentally [10, 11, 17–20]. However, the broadening G^- mode from

metallic SWNTs is not necessarily observed by Raman spectroscopy. This is because the strength of electron-phonon coupling, reflected by the intensity and the full-width at half-maximum (FWHM) of G^- mode, is sensitive to many factors, like the position of Fermi energy (E_F) [11]. When the metallic SWNT is sufficiently biased at either positive or negative potential through electrostatic gating, the E_F is moved far from the Dirac point, thus blocking the low-energy vertical electronic transitions [11]. Besides, E_F shift is also realized by doping and chemical functionalization of SWNTs [21], causing a high degree of variation in the broadening of G^- mode.

Besides the position of Fermi energy, the measurement temperature is also reported to affect the profile of Raman spectra [22–27]. With the increase of temperature, the peak position shifts to lower frequency due to the softening of the C-C bond [25–27]. Based on the frequency downshift, the temperature coefficient, which reflects the thermal stability of SWNTs, can be deduced [25–27]. However, the temperature evolution of G^- mode, which is an indication of the strength of electron-phonon coupling, has rarely been reported [23]. Uchida et al. [23] studied the G band in Raman spectra of bundled SWNTs and found that the line width of the BWF mode decreases with increasing temperature. They attributed the temperature-dependent behavior of BWF line to the bundling effect, which affects the formation of plasmon band. However, as phonon energies of G mode (~0.2 eV) and RBM (~0.02 eV) are different, in the case of scattering resonance, the Raman responses of G mode and RBM are not necessarily from the same SWNTs, ruling out the possibility of establishing an evolution correlation between them. To circumvent the problem, temperature-dependent Raman spectra of SWNTs grown either on the surface or across trenches are investigated [24, 28]. In such a case, incident resonance where both the RBM and G mode arising from the same SWNT occurs. The temperature coefficients (α) for the different peaks, including RBM, G^-, G^+, and G', are therefore unambiguously determined. For example, Zhang et al. [28] measured the temperature coefficients of 13 SWNTs and found that α_{RBM} depends on both SWNT diameter and chirality. Despite overall progress, investigation on the temperature-evolution correlation between SWNT RBM and G^- mode remains lacking.

In the work reported here, we present a systematic study on the temperature-dependent Raman spectra of surface-grown metallic SWNTs. By following the evolution of Raman spectra acquired at different temperatures, a correlation between the intensities of RBM and G^- mode is established, where a simultaneous change in the RBM and G^- intensities is observed. Such a result could be explained based on the temperature-induced shift of optical transition energy (E_{11} for the metallic SWNTs in our experiment) and resonance effect.

1.1. Experimental. SWNTs were synthesized in a vertical chemical vapor deposition system using a CO catalyst, which had been sputtered onto a SiO_2 substrate using an agar sputter coater. After being heated to the desired temperature, CO was introduced as the carbon source and the reaction lasted for 30 min. Detailed procedure for SWNT synthesis is described elsewhere [29].

Raman measurements on the SWNTs were carried out with a JY LabRAM HR 300 using 1.96 eV (633 nm) Ar ion laser excitation source. Temperature-dependent Raman spectra were recorded in a Linkam CCR1000 heating stage with a controlled environment sample chamber. Samples were heated or cooled to the desired temperature at a rate of 20°C/min under a continuous Ar flow (50 cm^3/min). After reaching the desired temperature, the hot stage was stabilized for more than 10 min to ensure that the temperature of the hot stage was the same as the sample. Prior to Raman measurements, the SWNTs were annealed in Ar at 450°C for 60 min to minimize gas absorption from the ambient environment. Laser power was kept at ~10 μW to avoid the heating effect of the laser.

2. Results and Discussion

Figure 1(a) presents a scanning electron microscope image of SWNTs grown on a SiO_2 substrate. SWNTs with lengths of several μm and a density of 3–8 tube/μm^2 were synthesized. Figure 1(b) shows a typical Raman spectrum of as-produced SWNTs. A characteristic RBM peak of SWNT centered at 192 cm^{-1} is observed. According to Kataura et al.'s plot [9], such a SWNT can be assigned as a metallic one. However, high-energy modes around 1600 cm^{-1} (G^- and G^+) exhibit typical Lorentzian line shapes without the appearance of a broad and soft G^- peak. Such a result is in agreement with many previous reports where BWF lines were not necessarily observed in the Raman spectra of individual metallic SWNTs [3]. In our sample, most of the observed RBMs are located in the range of 150 cm^{-1} to 265 cm^{-1}, corresponding to SWNT diameters ranging from 0.9 to ~1.7 nm.

To study the temperature-dependent behavior of G^- mode in metallic SWNTs, we performed the Raman characterizations on SWNTs at different temperatures. As O_2 adsorption on a SWNT surface could shift the position of Fermi energy [30] and complicate the analysis, the sample was preannealed in Ar to eliminate possible molecular adsorption [13]. Figure 2 depicts the Raman spectra acquired at three different temperatures from two spots of the sample surface. In both cases, only one RBM correlated with metallic SWNT is observed and the high-energy mode displays one G^- peak and one G^+ peak. As the resonance window of the G mode is wider than that of the RBM mode [2], besides the RBM-correlated metallic SWNTs, other SWNT species, including semiconducting SWNTs, could contribute to the G mode. As revealed by Fouquet et al. [10], the G^+ peak is assigned to the longitudinal mode of the semiconducting tube and the G^- peak is assigned to the longitudinal mode of the metallic tube.

From the temperature-dependent profiles of G mode (Figure 2), we can clearly see that, with increased temperature, the profile of G^+ mode shows negligible change except for the frequency downshift arising from temperature-induced C-C bond softening [24, 28]. In contrast, the relative intensity and profile of G^- show striking differences at different temperatures. Figure 2(a) shows that the broadening and

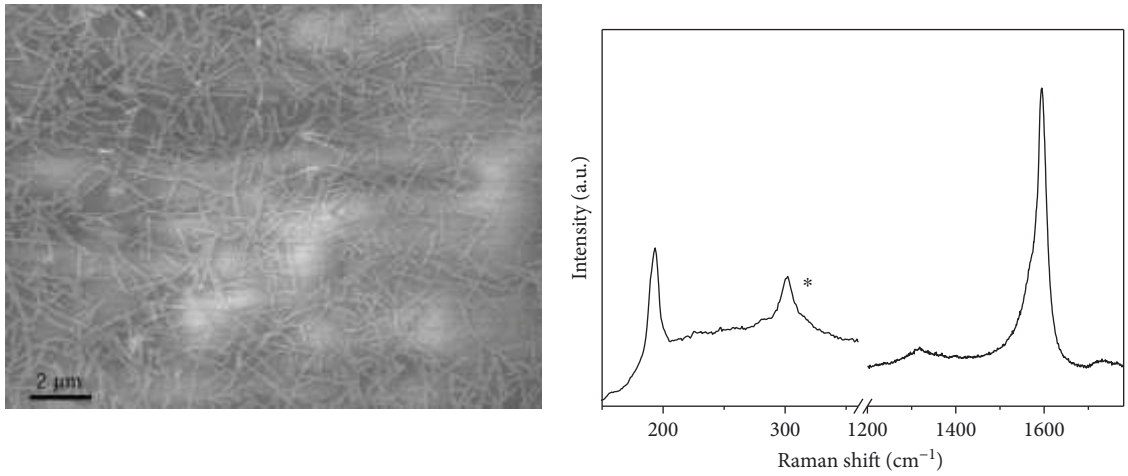

FIGURE 1: (a) Scanning electron microscope image of SWNTs. (b) A typical Raman spectrum acquired at room temperature. The peak marked with an asterisk is from the substrate.

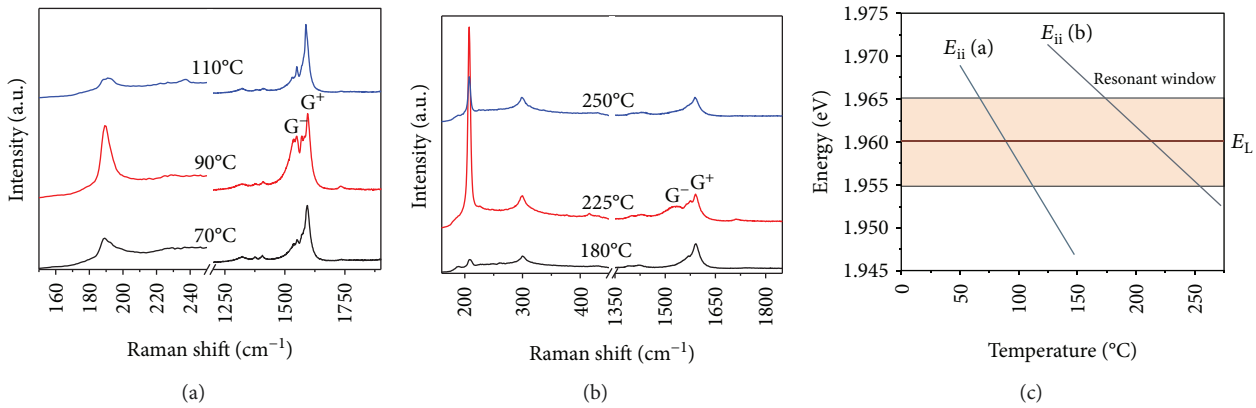

FIGURE 2: (a, b) Evolutions of RBM mode and G mode with increasing temperature. Spectra were acquired from two different spots on the substrate at temperatures listed above each spectrum. (c) Schematic illustration of the resonance conditions as a function of temperature-induced change of E_{ii} for two SWNTs shown in (a) and (b). E_L denotes the excitation laser energy, and the orange zone marks the resonance window where RBMs of SWNTs can be observed.

softening of G$^-$ peak are not significant for the Raman spectrum acquired at 70°C. When the temperature reaches 90°C, a broad G$^-$ peak with a high intensity appears, suggesting a strong electron-phonon coupling. Further increasing the temperature to 110°C diminishes the broadening characteristic of G$^-$ peak. A similar trend is observed for the Raman spectra displayed in Figure 2(b). Only at a fixed temperature (225°C) can a soft G$^-$ mode with a high intensity be observed. Interestingly, the intensity of G$^-$ peak is synchronized with the RBM intensity, which reaches the maximum at 90°C for SWNT as depicted in Figure 2(a) and at 225°C for SWNT as depicted in Figure 2(b). The variation of the RBM intensity is correlated with the temperature-induced change of E_{ii}. Generally, E_{ii} is downshifted with increasing temperature [31, 32]. At a low temperature, the transitional energy E_{ii} of the metallic SWNT is slightly larger than the excitation laser energy (E_L), and the RBM shows modest intensity. When raising temperature, the E_{ii} decreases towards E_L, resulting in a strong RBM peak. Excessively increasing temperature separates E_{ii} from E_L again, causing a decrease in RBM intensity. Schematic illustration of the change of resonance conditions as a function of temperature is shown in Figure 2(c). Such a resonance condition change can also explain the simultaneous intensity change of G$^-$ mode, which originated from the longitudinal mode of metallic SWNT. More importantly, the results suggest that under weak resonance condition, the intensity and broadening of G$^-$ peak are not significant. Such a finding could partially account for the lack of a broad and soft G$^-$ mode in the Raman spectra of some metallic SWNTs reported previously [33].

Figure 3(a) shows the Raman spectra of SWNTs acquired at temperatures ranging from 500°C to 650°C on one sample spot. Although two RBM peaks (182 cm^{-1} and 190 cm^{-1}) are observed at a low temperature range, the one centered at 190 cm^{-1} diminishes with increasing temperature and contributes little to the G$^-$ mode. Consequently, we only discuss temperature evolution of the RBM centered at 182 cm^{-1} and the G mode here. The RBM is almost invisible at 500°C,

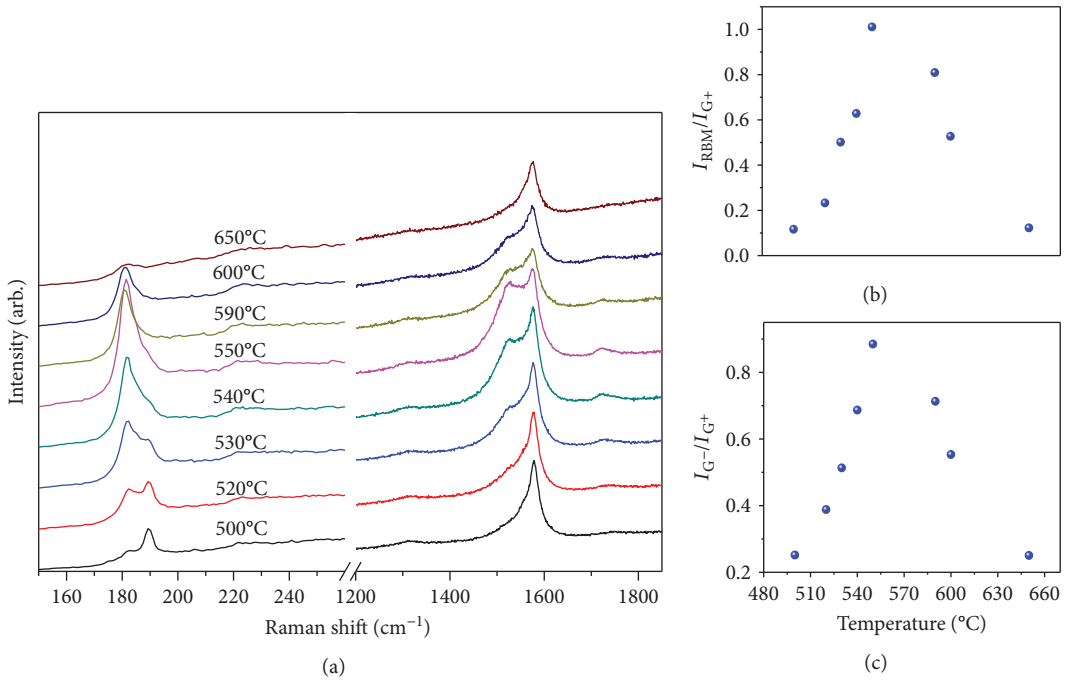

FIGURE 3: (a) Temperature dependence of the RBM and G mode in Raman spectra. (b, c) Temperature-dependent intensity ratio of RBM to G^+ band and intensity ratio of G^- band to G^+ band.

indicating that the tube is out of resonance and E_{ii} of the metallic nanotube is much larger than E_L. Increasing temperature decreases the E_{ii} of the tube, which falls into the resonance window and accounts for the appearance of RBM. When increasing the temperature from 500°C to 550°C, E_{ii} becomes smaller and the difference between E_{ii} and E_L decreases. As a result, the scattering cross-section of Raman signal is getting larger, an intensity maximum is achieved at 550°C where E_{ii} matches E_L well. However, further decreases of E_{ii} with increasing temperature leads to a gradual decrease in the intensity of RBM peak (550–650°C). At a temperature of 650°C, the tube is out of resonance with E_L and the RBM vanishes. Assuming the incident resonance window for the isolated SWNT is ~10 meV [3], the appearance of the RBM in the temperature window of 500°C~650°C gives a downshift coefficient of E_{ii} on the order of 67 μeV/K, well within the range calculated by Capaz et al. [31]. In addition, the resonance window for observing a soft G^- is estimated to be less than 5 meV (from 530°C to 600°C).

Unlike the RBM intensity evolution with temperature, the intensity of G^+ peak, mainly arising from the contribution of semiconducting SWNTs [10], does not exhibit dramatic change when modulating the temperature. To normalize the RBM peak and analyze its intensity change with temperature, we plotted the intensity ratio ($I_{RBM}/I_G{}^+$) as a function of temperature (Figure 3(b)). Clearly, a maximum ratio of 1.01 is observed at 550°C. In both sides of the point, the intensity ratio gradually decreases. A similar behavior is detected for the G^- mode. It is noted that the change trend of full-width at half-maximum (FWHM) is similar to the change of the intensity. For simplicity, only the intensity of G^- is discussed here. Figure 3(a) shows that the intensity of G^- peak demonstrates striking differences when raising temperature. The normalized intensity ratio ($I_G{}^-/I_G{}^+$) is also plotted against the temperature (Figure 3(c)). Obviously, the change of $I_G{}^-/I_G{}^+$ intensity ratio is related to the resonance conditions, which occurs simultaneously with the resonance scattering process of RBM. As the intensity and width of G^- mode are indications of the strength of electron-phonon coupling [11, 12], when the E_{ii} of the metallic tube matches E_L, an increase in electron-phonon coupling is well suggested.

Based on the observations, the intensities of both RBM and G^- mode show similar trends when changing temperature, which modifies the E_{ii} of the tubes. Such observations have three immediate implications. The first is related to the use of peak intensity ratios (RBMs or high-energy mode from metallic and semiconducting SWNTs) to evaluate the selectivity of semiconducting or metallic SWNTs in bulk products. Caution should be paid when using the intensity (or area) ratio to determine the selectivity of SWNTs with different conductivities. Independent verification from other approaches, like electrical property measurement or electron microscopy technique, is necessary to make reliable conclusions. Second, it is possible to tune E_{ii} by changing temperature, thus offering more opportunity to detect different SWNT species with only one available fixed Raman laser wavelength. Third, changing the Raman characterization temperature provides an alternative solution for recovering the broad and soft G^- mode in individual metallic SWNTs.

In conclusion, in agreement with theoretical predications, E_{ii} of metallic SWNTs is observed to decrease with increasing temperature. Taking the resonance window for

isolated SWNT of ~10 meV into account, the change of E_{ii} with temperature is estimated to be several tens of μeV/K. More importantly, both RBM intensity and G^- mode intensity are demonstrated to depend on the resonance conditions, that is, the match between E_{ii} and E_L. Only when E_{ii} well matches with E_L can a strong G^- with a large FWHM be observed. This work not only confirms that the G^- mode mainly arises from metallic SWNTs but also establishes a correlation between the intensities of RBM and G^- mode, which would help gain more insights in understanding the Raman spectra of metallic SWNTs.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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