Temperature dependence of the Raman spectra of single-wall carbon nanotubes

Department of Physics, Peking University, Beijing 100871, People's Republic of China

Z. J. Shi and Z. N. Gu
Department of Chemistry, Peking University, Beijing 100871, People's Republic of China

B. B. Liu, R. S. Yang, H. B. Yang, and G. T. Zou
National Laboratory of Superhard Materials, Jilin University, Changchun 130023, People's Republic of China

Y. Zhang and S. Iijima
Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

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Raman spectra of single-wall carbon nanotubes (SWCNTs) were measured at different temperatures by varying the incident laser power. The elevated temperature of the SWCNTs and multiwall carbon nanotubes (MWCNTs) is confirmed to be due to the presence of impurities, defects, and disorder. The temperature coefficient of the frequency of the C–C stretching mode \( E_{2g} \) (GM) and that of the radial breathing mode in the SWCNT were determined to be ~ 0.038 and ~ 0.013 cm\(^{-1}\)/K, respectively. It is found that the temperature coefficient of the GM in the SWCNT is larger than that of the MWCNT, highly oriented pyrolytic graphite, and the graphite. This is attributed to the structural characteristic of the SWCNT—a single tubular carbon sheet with smaller diameter.

Raman spectroscopy is a nondestructive technique for structural characterization of many materials. In recent years, Raman spectra of carbon nanotubes (CNTs) have attracted a lot of attention, both theoretically and experimentally. Both multiwall carbon nanotubes (MWCNTs) and single-wall carbon nanotubes (SWCNTs) have been studied. Temperature-induced changes in the vibrational bands of carbonaceous materials including carbon fiber, highly oriented pyrolytic graphite (HOPG), disordered carbon, and more recently, MWCNTs, were investigated using Raman spectra. In our previous report, we have systematically studied the temperature effect induced by laser heating of MWCNTs and other materials such as active carbon (AC), HOPG, and diamond. We found that increases of the incident laser power induced corresponding increases in the temperature of MWCNTs and AC, but not for HOPG and diamond. In addition, the Raman peak position of the optical C–C stretching mode \( E_{2g} \) (GM) of the MWCNT and AC at ~ 1585 cm\(^{-1}\) shifts to lower frequency with increasing temperature. In this letter, we report further studies on the laser-induced heating and temperature-reduced effect of the Raman shift of CNTs and its origin to also include study on SWCNTs.

The SWCNT samples were synthesized by the arc-discharge method. The transmission electron microscopy image of a purified sample is shown in Fig. 1. As seen in the image, most SWCNTs in the sample have a diameter of 1.3–1.4 nm and they tend to self-organize into bundles. All Raman spectra were measured in a backscattering geometry by a Renishaw 1000 Raman microscope with a Linkam THMS600 heating stage. The 514.5 nm line of an Ar\(^+\) laser was used as the excitation. The laser power ranged from 50 \( \mu \)W to 5 mW at the sample and was focused into a spot size of 1–2 \( \mu \)m in diameter, giving a power density of \( 10^2–10^4 \) W/cm\(^2\). The sample temperature of the measured spot was determined \textit{in situ} by the ratio of the intensity of the Stokes and anti-Stokes Raman peaks.

Our previous study reported the laser-induced temperature increase in the MWCNT and AC, but not in HOPG and diamond, suggesting that the ability to induce the temperature increase in carbonaceous materials may originate from the presence of impurities, defects, and disorder in the samples. In order to confirm this explanation, we measured the temperature of unpurified SWCNTs, purified SWCNTs,
and Au-ion implanted HOPG (Au–HOPG) by laser-induced heating. The Au ions were implanted with a dose of $10^{15}$ ions/cm$^2$ at an accelerating voltage of 100 keV. Clearly, ion implantation introduces impurities, defects, and disorder into the HOPG. Furthermore, the density of impurities in purified SWCNTs is lower than that in unpurified ones. Figure 2 shows the temperature increase of the samples with increasing the laser power. As seen in Fig. 2, the temperature of the Au–HOPG increases with increasing the laser power, and the same laser power induces a higher temperature in the unpurified SWCNTs than that in purified SWCNTs. Recalling that no temperature increase with increasing the incident laser power for HOPG, the results confirm that the ability of laser-induced heating of these carbonaceous materials depends on the presence of impurities, defects, and disorder with high density.

CNTs synthesized by the arc-discharge method inevitably contain many impurities (other carbonaceous materials, e.g., C$_60$, disorder carbon, etc.), defects (such as some polyhedral defects in the cap of squat SWCNTs), and disorder (tangling with each other) in the final product. The impurity, defect, and disorder presence reduces the thermal conductivity of the CNTs sample significantly, resulting in the thermal conductivity usually being much lower than that of the HOPG and diamond. The high thermal conductivity of HOPG and diamond allows the samples to dissipate laser-induced heating effectively, resulting in minimal to no increase in sample temperature. In contrast, the lower thermal conductivity in CNTs makes heating dissipation inefficient. Therefore, it is expected that the temperature of CNTs samples appears to increase with increasing laser power, as shown in Fig. 2.

Figure 3 shows the change of the Raman spectra of the SWCNT at different temperatures due to laser illumination. With increasing temperature the wave numbers of the Raman peaks downshift simultaneously. Note that changes occur not only in the GM of the optical phonons, but also in the radial breathing mode (RBM) of the acoustic phonons centered at about 180 cm$^{-1}$ that is not observed in the MWCNTs. The result, together with that of the MWCNTs, indicates that the strong temperature effect is a common property of all CNTs. It is shown in Fig. 3 that the Raman peak of optical mode GM at $\sim$1585 cm$^{-1}$ observed in the MWCNT, splits into three distinguishable peaks at $\sim$1550, 1567, and 1590 cm$^{-1}$, respectively, in the SWCNT, which was also reported in Ref. 13. In this letter, we only discuss the dominant peak at 1590 cm$^{-1}$. The Raman peak positions of the GM and RBM of the SWCNTs as a function of temperature are shown in Fig. 4. The straight lines are linear least-square fits. Table I lists the slopes (i.e., temperature coefficient of Raman frequency shift) and the intercepts of the fitted straight lines. The values of the MWCNTs, graphite, and HOPG (Ref. 5) are also listed in Table I for comparison. Electric heating was also carried out in a Linkam TH600 heating stage to study the effect of temperature on the Raman spectra of the CNTs. The results are presented in Fig. 4 and listed in Table I. As shown in Fig. 4 and Table I, the downshifts of the GM and RBM frequencies induced by electric heating are basically identical to those by the laser illumination. It indicates that the frequency change of GM and RBM under laser illumination originates from the laser-induced heating effect.

![Fig. 2. Temperatures calculated from Raman peaks of the unpurified, purified SWCNT, and Au–HOPG as a function of incident laser power.](image1.png)

![Fig. 3. Raman spectra of the SWCNT between 150 and 225 cm$^{-1}$ and between 1400 and 1700 cm$^{-1}$ at temperatures of 435, 500, and 600 K, respectively.](image2.png)

![Fig. 4. Temperature dependence of the frequencies of the GM and RBM for SWCNTs heated by laser (marked by the symbol "▲" and solid fitted lines) and by a Linkam TH600 stage (marked by the symbol "○" and the dashed fitted line).](image3.png)
According to the temperature coefficients of the GM frequencies shown in Table I, the value of the SWCNT is significantly larger than that of the MWCNT, HOPG, and graphite, and the latter have a basically identical value. As discussed in previous literature, the frequency downshift of the GM in the above carbonaceous materials is associated with the lengthening of the C–C bond. The longer bond length results from the thermal expansion of the material upon the temperature increase. To seek the origin of the different temperature coefficients, we think that it is easier to lengthen the length of the C–C bonds for the SWCNT than for the MWCNT, graphite, and HOPG under the same changing temperature. It may be attributed to the difference in structures among these carbonaceous materials.

An ideal SWCNT is formed by a planar graphene sheet rolled up into a seamless, cylindrical tube. Because of the curvature, when the C–C bonds on the cylindrical tube stretch the restoring force will have a new radial component, which is proportional to the curvature of the cylindrical tube, except that it is in the direction of the C–C bond. As a result, the expansion in the tangential direction of the SWCNT is weakly restricted compared to that in planar graphite and one would expect the C–C bond of the SWCNT to be easily expanded with increasing temperature. As for the GM, which is due to the displacement of adjacent carbons in the C–C bond direction, it is anticipated that the curved SWCNT should have a larger temperature coefficient for the GM shift than the planar carbon materials, such as the graphite and HOPG. Furthermore, the expansion of C–C bonds will induce an increase of SWCNT diameter upon increase in temperature. Then, it should also be expected to have a higher temperature coefficient of the RBM, which is due to the vibration in the radial direction. Since MWCNTs are a multiple-layer structure, and have an inner and outer diameter range of 10–50 nm, one order of magnitude larger than the diameter (1–2 nm) of SWCNTs, the structural effects on the vibration properties for MWCNTs are much closer to those of planar graphite than to those of SWCNTs, although both the SWCNT and MWCNT are tubular materials. In fact, our results in Table I show that the curvature effect MWCNT is negligible, giving a temperature coefficient comparable to that of graphite.

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**TABLE I.** Slopes and intercepts of the fitted straight line for the GM and RBM of the SWCNT in Fig. 2 and the reported results of the MWCNT, graphite (Lonza Kr-5-75) (GL), and HOPG.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser</th>
<th>Heating stage</th>
<th>MWCNT*</th>
<th>GL*</th>
<th>HOPG*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (10⁻² cm²/K)</td>
<td>GM</td>
<td>−3.8</td>
<td>−4.2</td>
<td>−2.8</td>
<td>−3.0</td>
</tr>
<tr>
<td>Intercept (cm⁻¹)</td>
<td>GM</td>
<td>1606</td>
<td>1609</td>
<td>1611</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RBM</td>
<td>193</td>
<td>192</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aPresent work.
*bReference 9.
*cReference 4.
*dReference 5.