Chirality-Dependent Raman Frequency Variation of Single-Walled Carbon Nanotubes under Uniaxial Strain

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By using a homemade setup, the length of uniaxial strained single-walled carbon nanotubes (SWNTs) was directly measured by scanning electron microscopy (SEM), and quantitative relations between uniaxial strain and Raman frequency were obtained. It was found that RBM frequency was not affected, but $G$-band frequency variation was diameter and chirality-dependent under uniaxial strain. The $G$-band frequency shift rate increased with diameter increasing and chiral angle decreasing. Also $G^+$ and $G^-$ frequency shift rates were related to chiral angle due to chirality-dependent $C-\text{C}$ bonds elongation. A surprising finding that intermediate frequency mode (IFM) frequency upshifted with uniaxial strain increasing indicates that lattice transformation needs to be considered in phonon properties under uniaxial strain. These studies provide valuable information about geometric structure variation of SWNTs under uniaxial strain.

Introduction

The electronic structure and chemical and physical properties of single-walled carbon nanotubes (SWNTs) uniquely depend on their chiral indices $(n,m)$. This also applies to their response to uniaxial strain, which is a hot topic in recent studies on SWNTs. Theoretical and experimental studies both revealed that the electronic structure of SWNTs can change significantly with uniaxial strain and follows the family pattern. A recent experimental study by Huang et al. directly measured the uniaxial strain-induced changes in the electronic structure of SWNTs and presented a revised relationship, which has an implication in the analysis of the coupling between the electronic system and any long-wavelength acoustic phonon.

Resonant Raman spectroscopy of SWNTs, which is closely related to their chiral indices, is a powerful tool in probing the geometrical structure in SWNTs. Theoretical calculations show that radial breathing mode (RBM) did not shift, but tangential $G$-band linearly downshifted with uniaxial strain increasing. There have also been several experimental studies concerning the uniaxial strain induced Raman frequency variation of SWNTs. However, due to indirect measurement and low precision of uniaxial strain, different relations between uniaxial strain and Raman frequency were given, and the dependence on chirality was not yet observed.

In this paper, the length of uniaxial strained SWNTs was directly measured by scanning electron microscopy (SEM) to obtain quantitative relations between uniaxial strain and Raman frequency, and thus the dependence of Raman frequency variation on chirality was first reported. New findings on Raman modes, including $G$-band, IFM and $D$-band, indicate lattice transformation needs to be considered in phonon properties under uniaxial strain.

Experimental Section

The experiment was carried out using a homemade stretching setup (see inset of Figure 1). By rotating a screw at the step of $30^\circ$, flexible polydimethylsiloxane (PDMS) was stretched and then uniaxial strain was introduced into suspended SWNTs gradually. The sample was prepared as follows (see Figure 1). SWNTs were grown on a SiO$_2$/Si substrate by catalytic chemical vapor decomposition (CVD) of ethanol. PDMS with trenches was prepared by pouring DMS on Si with patterns and heat curing. By pressing the SiO$_2$/Si substrate against flexible PDMS with trenches, some SWNTs were transferred to PDMS. Since the trench was 2.5 $\mu$m deep and 4 $\mu$m wide, most SWNTs were suspended.
were suspended in the trench. About 12 nm thick gold films were deposited onto the PDMS and SWNTs. Deposited gold films on PDMS could hold SWNTs in place and prevent suspended SWNTs slack. By laser heating at 100% of laser intensity (7 mW), gold films on PDMS and SWNTs evaporated and then recrystallized as gold particles on suspended SWNTs. These gold particles on suspended SWNTs were reference marks to measure the length of SWNTs directly and precisely, which is also a good prototype for surface enhanced Raman scattering (SERS) effect. At each uniaxial strain Raman spectral characterization (633 nm He–Ne laser) at 50% of laser intensity and subsequent SEM measurement (resolution better than 5 nm at 1 kV) were performed separately.

Results and Discussion

Figure 2A shows the SEM image of a suspended (18, 5) SWNT, uniaxial strain of which first increase and then decrease by stretching and relaxing PDMS. The length between two gold particles can be directly measured on the SEM image. It can be seen that the length between two gold particles first increases and then decreases linearly. Due to high resolution of SEM, the shift trend is opposite to other Raman modes. Previous studies attributed the uniaxial strain induced downshift of Raman modes to elongation of C–C bonds, which weakened C–C bonds. Obviously, this explanation cannot apply to IFM. It does not shift (see Figure S2 in Supporting Information), but both $G^+$ and $G^-$ downshift linearly at a rate of $-3.95 \text{ cm}^{-1}/\%$ and $-1.89 \text{ cm}^{-1}/\%$ (see Table 1). The shift rate of $G^+$ is much larger than that of $G^-$, about twice as that of $G^-$. Hence, as shown in Figure 3B, the peaks of $G^+$ and $G^-$ are closer and closer with uniaxial strain increasing. The difference in relative shift rate between $G^+$ and $G^-$ is probably because the unit cells of graphene arrange along different directions relative to the SWNTs axis.

Table 1: Uniaxial Strain Induced Raman Frequency Variation of 7 Individual SWNTs

<table>
<thead>
<tr>
<th>RBM (cm$^{-1}$)</th>
<th>(n,m)</th>
<th>d (nm)</th>
<th>$\theta$ (°)</th>
<th>$G^+$ (cm$^{-1}/%$)</th>
<th>$G^-$ (cm$^{-1}/%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>(6,5)</td>
<td>0.76</td>
<td>27.00</td>
<td>-3.97</td>
<td>N/A</td>
</tr>
<tr>
<td>281</td>
<td>(7,5)</td>
<td>0.83</td>
<td>24.50</td>
<td>-3.95</td>
<td>-1.89</td>
</tr>
<tr>
<td>213</td>
<td>(11,5)</td>
<td>1.13</td>
<td>17.78</td>
<td>-6.50</td>
<td>N/A</td>
</tr>
<tr>
<td>177</td>
<td>(14,5)</td>
<td>1.35</td>
<td>14.70</td>
<td>-6.43</td>
<td>N/A</td>
</tr>
<tr>
<td>171</td>
<td>(13,7)</td>
<td>1.40</td>
<td>20.17</td>
<td>-13.06</td>
<td>-11.80</td>
</tr>
<tr>
<td>146</td>
<td>(18,5)</td>
<td>1.66</td>
<td>11.93</td>
<td>-14.59</td>
<td>-11.00</td>
</tr>
</tbody>
</table>

*d: diameter; $\theta$: chiral angle; (n, m) are assigned from RBM frequency; d and $\theta$ are calculated from (n, m). N/A means that the peaks are not observed.

As shown in Figure 3, for (7, 5) SWNT, similar results are observed. When uniaxial strain increases from 0 to 7.1%, RBM frequencies variation as a function of uniaxial strain. Here $\omega_{G^+}$ and $\omega_{G^-}$ are the unstrained and strained frequency respectively. The shift rate of $G^+$ is probably because the unit cells of graphene arrange along different directions relative to the SWNTs axis.

Figure 3. (A) SEM image, (B) $G$-band spectra and (C) IFM spectra of (7, 5) SWNT when uniaxial strain increase from 0% to 7.1%. (D) $G^+$, $G^-$ and (E) IFM frequencies as a function of uniaxial strain; lines are linearly fitted from experimental data which are obtained by Lorentzian fitting.

TABLE 1: Uniaxial Strain Induced Raman Frequency Variation of 7 Individual SWNTs
It is noted that there are no D-band occurring even 7% uniaxial strain for (7, 5) SWNT (see Figure S4 in Supporting Information). It is known that D-band is centered at ∼1300 cm⁻¹ and is originated from disorders in SWNTs, such as dangling bond, 5–7 ring, sp³ hybridization or edge effect. D-band is not observed in all uniaxial strained SWNTs. Our observation is not consistent with Lee’s finding: in some uniaxial strained SWNTs a small and sharp D-band occurred at a very small uniaxial strain, e.g., 0.004%. No occurrence of D-band means that SWNTs possess excellent elastic property and uniaxial strain only induces lattice transformation which can be recovered when uniaxial strain is relaxed.

**Conclusion**

In conclusion, we measured the quantitative relations between Raman frequency and uniaxial strain of SWNTs, and found that the variation of Raman frequency was strongly dependent on their chirality. This finding can help us know geometric structure variation of SWNTs under uniaxial strain. Another direct implication of this study is in the analysis the SWNTs enhanced composites. Precise relations between Raman frequency and uniaxial strain can bring a simple and accurate method of characterizing uniaxial strain in the research and application of composites. Also, our study presents a novel and universal experimental scheme for the research of one-dimensional nanowires and other nanomaterials.

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**Supporting Information Available:** The variation of RBM (Figure S1 and S2) and D-band spectra (Figure S4) under uniaxial strain; D-band during repetitious measurement experiment (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


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