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Raman study of bromine-doped single-walled carbon nanotubes under high pressure

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Abstract

Raman results for different single-walled carbon nanotube bundles doped with Br₂ were studied both at ambient pressure and under high pressure up to 6 GPa. Our study indicates that bromine resides in the interstitial channel of nanotube bundles as a form of polymer.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The physical properties of single-walled carbon nanotube (SWNT) bundles doped with halogens and alkali metals exhibit large differences with respect to the undoped pristine material. Raman spectroscopy is a powerful probe for studying the structure of doped SWNT bundles. Raman spectra for pristine SWNT samples are composed of two kinds of fingerprint mode: tangential modes (TMs) at 1590 cm⁻¹ which are related to the E_{g2} graphite mode, and breathing (radial) modes in the low-frequency range near 180 cm⁻¹ which are inversely proportional to the tube diameter. In the Raman spectra for SWNT samples doped with I₂, the breathing modes of SWNTs are invisible and vibrations for polyiodide are found in the low-frequency range. A linear polyiodide chain residing *inside* the tubes was recently evidenced by STEM images [1–3]. Kataura *et al* [4] reported a mode near 240 cm⁻¹ for Br₂-doped SWNTs with excitation energy higher than 1.8 eV and tentatively assigned it to the breathing mode of partially Br₂-doped nanotube bundles. Bromine has properties similar to those of iodine; however, the structure of bromine and where bromine locates in SWNT bundles are still not clear. The effect of hydrostatic pressure (HP), which induces a distortion in the cross-section of SWNTs and makes the breathing mode invisible at 1.5 GPa in pristine SWNT samples [5], gives us a further possibility for understanding the characteristic properties of doped SWNT samples. We present here Raman results for three SWNT samples doped with Br₂ both at ambient pressure and under high pressure. Our study indicates that bromine resides in the interstitial channel of nanotube bundles as a form of polymer.

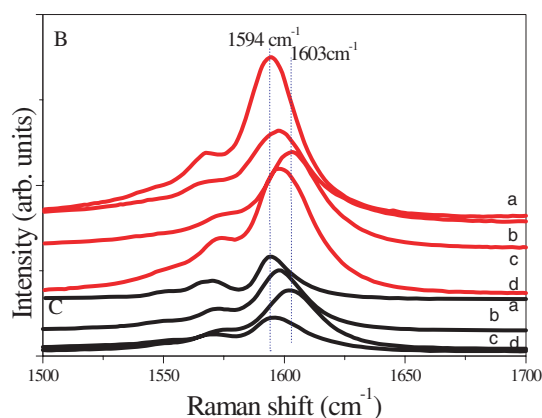


Figure 1. The high-frequency vibrations (TMs) in Raman spectra for Br₂-doped samples (B) produced in Umeå and (C) at Rice University; (a) the pristine sample, (b) doped with Br₂ for 1–2 min, (c) doped with Br₂ over 12 h and (d) dedoped at 210 °C for 2 h.

2. Experimental details

SWNTs were prepared by both arc evaporation and laser ablation methods. Sample A was produced by the arc method using Ce/Ni as a catalyst in He gas. It contains small-diameter and chiral tubes [6]. Two other samples were made by laser ablation using a second-harmonic Nd:YAG laser pulse. Sample B was produced in Umeå using a 2.6 at.% Ni/Co as catalyst in Ar gas while sample C was obtained from Rice University (Tubes@Rice Inc.). Samples A and B were as-grown mats while sample C was a mat made from a SWNT suspension. Suspension C was purified without amorphous carbon particles. The doping effect on this sample rules out any contribution from graphite intercalation compound.

Bromine-doped SWNT samples were obtained by introducing bromine into a quartz vessel containing nanotubes at room temperature after evacuation. Raman spectroscopy was performed using a Renishaw 1000 spectrometer with an excitation laser line of 514.5 nm from an Ar⁺ laser. High-pressure Raman spectra were measured in a diamond anvil cell up to 6 GPa with CsBr as a pressure medium and ruby as pressure calibrant.

3. Results and discussion

Under ambient pressure, Raman spectra for all three samples doped with bromine are very similar. In the high-frequency range, the TM at 1594 cm⁻¹ gradually shifts to high frequency and reaches 1603 cm⁻¹ when bromine is doped for over 12 h. Figure 1 shows these modes for samples B and C. The blue-shift of the TM is in agreement with the donation of charge from carbon tubes to bromine as an acceptor reported by other groups [3, 4]. Though the line shapes of TMs for the three pristine samples are different, the shifts of the TM are almost same. This result shows that the dopant has a similar effect on all these samples.

Figure 2 shows the Raman spectra in the low-frequency range. From the peak features for pristine samples (a), it is obvious that they have different tube diameter distributions. There is a strong peak at around 185 cm⁻¹ for all three samples. B has two extra peaks at 203 and 166 cm⁻¹ while A has one extra at 206 cm⁻¹. This implies that B has a broader tube distribution than A and that C has a very narrow tube distribution. For sample B doped for a long time, a very strong new peak at 240 cm⁻¹ and weak, broader peaks at lower frequencies are visible.

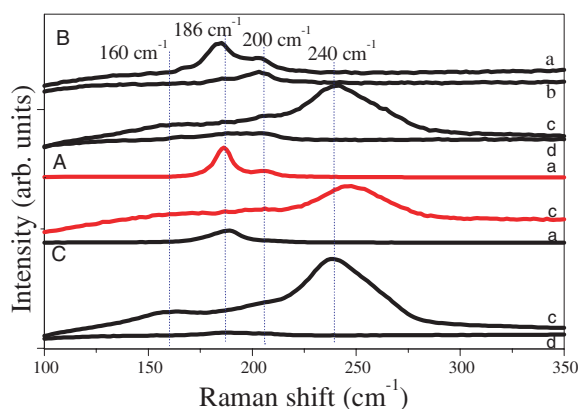


Figure 2. The low-frequency Raman spectra for Br_2 samples under ambient pressure. (A) Synthesized by the arc method. (B), (C) and (a)–(d) are the same as in figure 1.

Similar results are also found for samples A and C with quite different tube distributions. This suggests that the peaks at 240 cm^{-1} and lower frequency result from the doping effect of Br_2 and most probably are related to bromine. The peak at 240 cm^{-1} is also found in Br -graphite intercalation compounds and is assigned to bromine solid by many authors [7]. Because of the different tube diameter distributions, we assign 240 cm^{-1} to bromine solid and not to the breathing mode of the tubes.

For the sample doped with Br_2 for a short time, the main peak near 185 cm^{-1} decreases dramatically while the peak at 200 cm^{-1} decreases more slowly in intensity. With increasing doping time, this peak becomes weak but still exists. One example is sample B in figure 2 B (b) and B (c). However, a peak at the same position is observed for the pristine samples A and B. Though this peak is not very clear for pristine sample C, it cannot be assigned to bromine simply. This peak, found for all three doped samples, still needs further study.

We measured high-pressure Raman spectra for sample C doped with bromine. The sample was loaded in an inert gas atmosphere to avoid any reaction with air or water. The sample on which measurements were made under high pressure has no excess bromine due to slight evacuation of water and oxygen in the loading box. Figure 3 shows Raman spectra for the sample both outside and inside the diamond anvil cell. The peak around 200 cm^{-1} is clearly observed in the sample in the cell, similarly to the case for the sample doped for a short time at ambient pressure. The peak at 240 cm^{-1} , assigned to bromine solid, becomes weak. These features indicate that bromine solid probably resides in lower-binding-energy sites in the SWNT samples.

Figure 3 also shows the low-frequency Raman spectra under different pressures. The peak at 200 cm^{-1} gradually shifts with increasing pressure at a rate of $+7.6\text{ cm}^{-1}\text{ GPa}^{-1}$, similar to the rate of $8.1\text{ cm}^{-1}\text{ GPa}^{-1}$ for the TM in the same study and to data calculated from the breathing modes of pristine samples below 1.5 GPa reported by other groups [1]. At $P = 1.65\text{ GPa}$, a new peak appears suddenly at 235 cm^{-1} . At $P = 2.86\text{ GPa}$, it becomes the most intense one and a new broad one at 172 cm^{-1} is observed. Up to 6 GPa , these peaks increase strongly in intensity with little change in frequency. Note that the peak at 200 cm^{-1} still exists above 1.5 GPa . It becomes invisible above 2.86 GPa as it gradually overlaps with the new broad peak at 235 cm^{-1} .

Under pressure the nanotubes in the bundles are pressed closer together and their breathing modes at low frequency disappear near 1.5 GPa due to distortion of the cross-section in the

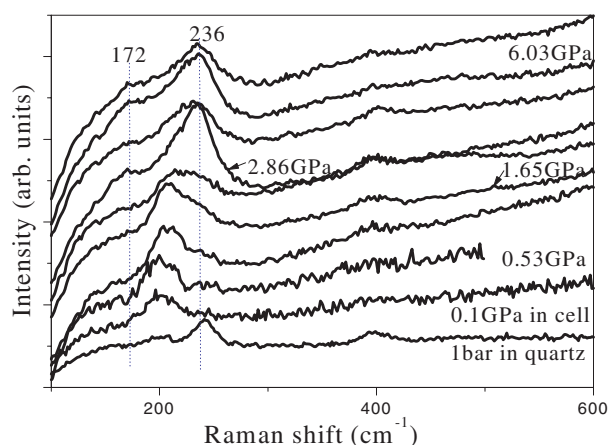


Figure 3. The low-frequency vibrations for SWNTs doped with Br₂ under high pressure up to 6 GPa with 514.5 nm excitation.

tubes [5]. The observation of the peak at 200 cm⁻¹ above 2 GPa indicates that this peak does not come from the breathing mode of the tubes, but from the vibration of bromine. The new peak at 235 cm⁻¹ and other peaks at lower frequencies observed above 1.5 GPa also result from the doping effect of Br₂ and are related to bromine complexes.

There are two possibilities for the form of bromine as dopant: bromine solid and polybromide. The peak at 240 cm⁻¹ is typical for bromine solid, while for polybromide, bands around 230 cm⁻¹ and some lower-frequency vibrations are attributed to stretching or anti-stretching modes of Br₃⁻ and Br₅⁻ polymers. The precise frequencies of these vibrations depend on the host material. In the Br-graphite intercalation compound, which is very similar to our system, the peak at 240 cm⁻¹ splits into three distinguishable peaks at 266, 292 and 300 cm⁻¹ at 1.2 GPa. In our experiment, the new peak at 235 cm⁻¹, observed at 1.65 GPa, changes little with pressure. We therefore suggest that the new peaks at 235 and 172 cm⁻¹ originate from polybromide chains because of the similarity with the known spectra of polybromides [8].

There are four types of site in our samples, including surface, groove, interstitial channel of bundles and inside of the tube. Calculations of binding energies in the hydrogen-SWNT system show that the energies of surface and groove sites are much lower than those interstitial channel and inside of the tubes [9]. We thus suggest that bromine solid mainly locates at the surface and groove sites where it is easily pumped away by a gentle evacuation.

As the new peaks were observed at 1.65 GPa, just at the pressure which induces a deformation of the tube cross-section, we suggest that bromine polymer resides in the interstitial channels in the bundles.

Acknowledgments

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