Structural transitions of SWNT filled with C_{60} under high pressure

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Raman spectra of C_{60} filled single-walled carbon nanotubes (C_{60}@SWNTs) with diameters of 1.3–1.5 nm have been studied under high pressure. A plateau in the pressure dependence of the G-band frequency at around 10 GPa was observed in both experiments with 514 nm and 830 nm excitation lasers, which is similar to the high pressure behaviors of pristine SWNTs. This structural transition has been assigned to the transformation into a peanut-like structure of the nanotubes. At pressure below 2 GPa, no obvious Raman signature related to the structural transition of nanotubes was observed, unlike what has been reported for C_{70} filled nanotubes. We discussed this point in terms of the arrangement differences of C_{60} and C_{70} molecules inside the nanotubes. At higher pressure up to 15 GPa, a graphite-like pressure evolution was observed in our C_{60}@SWNTs.

Keywords: carbon nanotubes, high pressure, Raman spectra

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1. Introduction

Carbon nanomaterials, especially single-walled carbon nanotubes and C_{60}, as important one-dimensional (1D) and zero-dimensional (0D) materials, have become an important object in the nanomaterial research field because of their unique structures and exotic physical and chemical properties.[1–3] It is theoretically predicted that Young's modulus of C_{60} is twice as large as that of diamond, up to 700–900 GPa,[4] thus C_{60} is considered as a potential superhard molecule. On the other hand, the single-walled carbon nanotube (SWNT) is considered as a one-dimensional material with a hollow tubular structure. It is hard at the axial direction with a very large modulus, but soft in the radial direction, so the single-walled carbon nanotube changes its structure under a low pressure. For example, the cross sections of SWNTs with diameters of 1.3–1.5 nm are changed at a critical pressure of approximately 2 GPa.[5,6] Therefore, it is expected that the C_{60}@SWNTs (SWNTs filled with C_{60}) peapod sample can serve as an ideal model of 1D superhard material[7] due to the supporting effect of the filled C_{60}s, and it is important to study its mechanical properties for fabricating 1D superhard material. High pressure is a powerful technique to study and tune mechanical and electronic properties of materials. Previous reports are mainly focused on the polymerization and rotating dynamics of the internally filled C_{60},[8–10] but little attention has been paid to the high pressure stability and structural changes in the host SWNT itself, probably due to limited knowledge about the structural transitions of pristine SWNT (no filling) under high pressure. Recently, a detailed study on the structural evolution of pristine SWNT under high pressure has been performed by our group using density functional theory calculations and high-pressure Raman spectra, and it was found that the structural evolution can be identified by the change of the Raman signal.[11] Recently, C_{70} filled SWNTs peapods and iodine filled SWNTs were studied by Raman spectra.[12–14] In sharp contrast to our expectations, it was found that the doped SWNTs collapsed even at lower pressure compared to pristine SWNTs, which may be caused by the inhomogeneous doping.[14] In addition, compared to the high-symmetric C_{60} molecules, the elliptical shape of C_{70} molecules and their arrangements of either standing or lying in the nanotube channel, may also affect the structural stability of the SWNTs under high pressure. At present, the detailed research on the high-pressure structural deformation of C_{60}-doped SWNTs has not been reported. In this paper, the effect of C_{60} doping on the structural evolution of SWNTs under high pressure is studied by Raman spectroscopy.

2. Experiment

SWNT samples used for doping in the experiment were synthesized by arc discharge, and purified by a procedure with oxidation and acid treatments.[15,16] The peapod samples were fabricated by a vapor phase diffusion method. Firstly, C_{60} powder (99.9%) and SWNT powder were mixed and heated to 823 K for 96 h. Then the mixed powder was cooled down to room temperature, followed by ultrasound in a toluene solution for 1 h to remove the C_{60} adsorbed on the outside surface of the nanotube. After drying, the highly pure peapod samples

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were obtained. A diamond anvil cell (DAC) with culet size of 500 μm was used to create high pressure. Methanol and ethanol mixture (volume ratio 4:1) was used as the pressure transmission medium and ruby was used for pressure calibration. Raman measurements were performed by a spectroscopy (Renishaw inVia) equipped with excitation wavelengths of 514 nm and 830 nm. The highest pressure reached in this study was 21.5 GPa.

3. Results and discussion

The high-resolution transmission electron microscopy (HRTEM) image of C_{60}@SWNTs is shown in Fig. 1. The peapod sample with high filling ratio of C_{60} can be observed in the image. The filling ratio is estimated to be higher than 80%.[8]

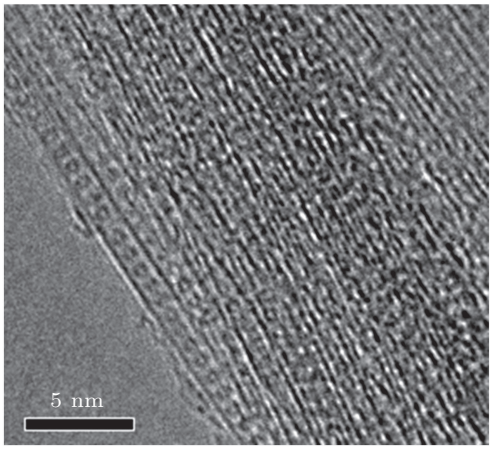


Fig. 1. HRTEM image of peapod sample.

The Raman spectra of the peapod samples measured at ambient pressure and high pressures are shown in Fig. 2. According to this figure, two characteristic vibration modes of SWNTs corresponding to radial breathing mode (RBM) at low frequency region (from 100 cm^{-1} to 300 cm^{-1}) and tangential vibration mode (TM) at high frequency region (from 1500 cm^{-1} to 1600 cm^{-1}) can be observed. Compared to pristine SWNTs, the RBMs of SWNTs filled with C_{60} show a red shift of 2–6 cm^{-1} in frequency, which may be caused by the expansion due to C_{60} filling in the SWNTs,[17] confirming that the SWNTs are indeed filled with C_{60}. The D band between 1300 cm^{-1} and 1400 cm^{-1} is caused by amorphous carbon and defects of nanotubes, and overlaps with the characteristic peak of diamond, so it will not be discussed in this paper. The G band of the SWNTs is located at $\sim$ 1580 cm^{-1}. In addition, the A_g vibration mode from the filled C_{60} is observed near 1460 cm^{-1}. Since the structural transitions of the filled C_{60} at high pressure has been reported in our previous work,[18] here we mainly concentrate on the Raman modes reflecting the structural evolutions of the host nanotubes under pressure.

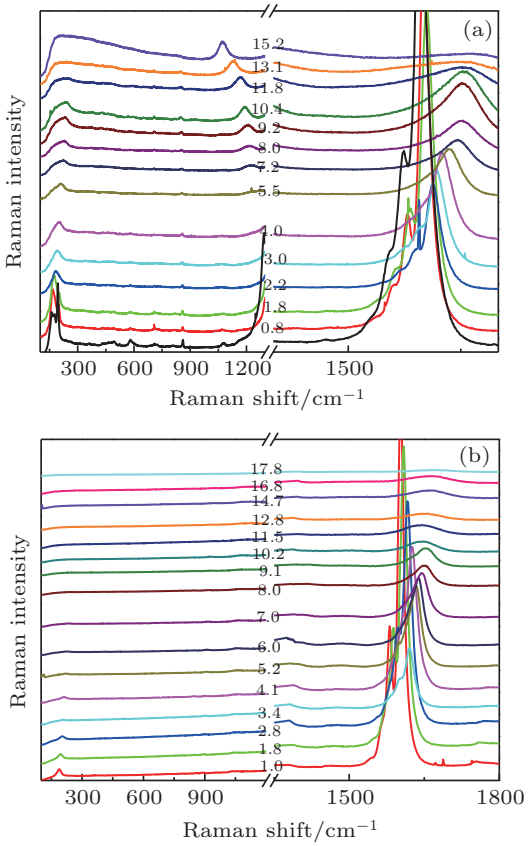


Fig. 2. (color online) Raman spectra of C_{60}@SWNTs peapod samples under atmospheric pressure and high pressures, with laser excitation wavelengths of (a) 830 nm and (b) 514 nm.

As the pressure increases, the RBM and G-band of the SWNTs gradually shift to higher frequencies, while the intensities gradually decrease, as shown in Fig. 3. As a result, the RBMs basically disappear at below 10 GPa, while G-band can be detected up to the highest pressure in this experiment, which is consistent with the behaviors of pristine SWNTs under high pressure. The pressure dependence of the RBM frequency is shown in Fig. 3(a). According to Fig. 3(a), with increasing pressure, the RBM shifts to higher frequency, and the relationship between the pressure and the frequency is nearly linear, with a slope $(\mathrm{d}w/\mathrm{d}p)$ of 6.7 ± 0.2 cm^{-1}/GPa. The FWHM variation of RBM with pressure is shown in Fig. 3(b), which can be used as evidence for the structural transition of the SWNTs.[11,14] It should be noted that the FWHM data of RBM above 4 GPa is not given here, due to the weakness of the RBM peaks above this pressure. According to Fig. 3(b), the FWHM variation is not obvious, different from the results observed in the C_{70} peapod samples. For the C_{70} peapod samples under high pressure, Caillier *et al.* observed that the FWHM of RBM increases obviously at around 2 GPa, and they explained it as the cross section of the SWNTs changes from circle to ellipse shape.[14] The frequency variation of G-band with pressure is shown in Fig. 4. Three stages can be observed in the curve. The first stage ranges from 0 to 8 GPa with a slope $(\mathrm{d}w/\mathrm{d}p)$ of 6.7 ± 0.2 cm^{-1}/GPa. The second stage is

a plateau ranging from 8 GPa to 13.5 GPa, which is almost pressure independent. The abnormal behavior has also been observed in empty SWNTs with different diameters. For the third stage observed at higher pressure, the frequency of G-band again increases with increasing pressure, but the slope ($\mathrm{d}w/\mathrm{d}p$) becomes smaller, close to that of graphite under high pressure.

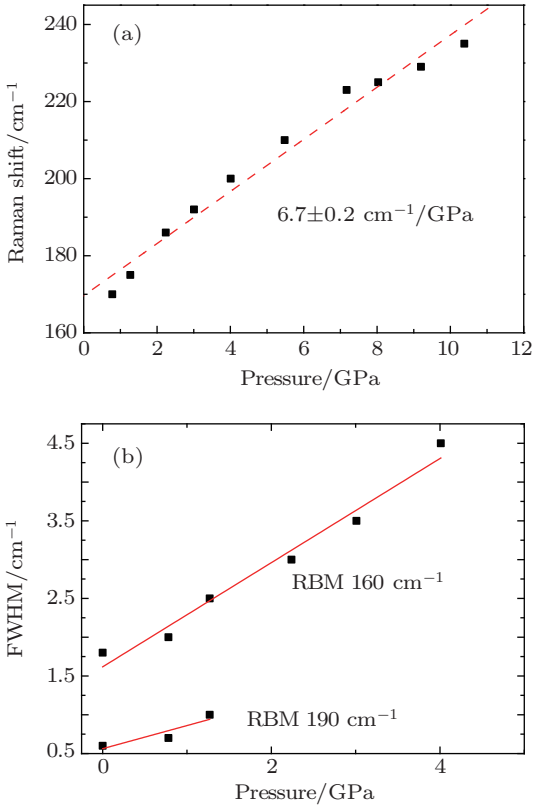


Fig. 3. (color online) (a) Pressure dependence of RBM frequency (initial frequency^{-1}) and (b) FWHM of RBMs of peapod sample. Excitation wavelength is 830 nm.

Firstly, we compare the results of SWNT samples filled with C_{60} with those of pristine SWNT sample under high pressure. For the pristine SWNT sample, the G-band plateau (frequency is independent of the pressure) is observed in the pressure range from 8 GPa to 14 GPa, while the curve of the RBM frequency as a function of pressure is linear.[11] Combined with the theoretical simulation, we suggest that the cross section of SWNT changes from oval to flat oval, and even to peanut-like shape. Interestingly, for the C_{60}@SWNTs peapod, the G-band plateau is observed in the pressure range from 8 GPa to 13.5 GPa, which is similar to that observed in the pristine SWNTs. We thus believe that a similar structural transition occurs in both samples in the plateau region.

Figure 4 shows the G-band frequency variation of the peapod sample with the pressure. The result is compared with that of compressing pristine SWNTs. According to this figure, the results with laser excitation wavelengths of 830 nm and 514 nm are the same. With increasing pressure, the slope ($\mathrm{d}w/\mathrm{d}p$) of the G-band frequency variation with pressure is 6.7 ± 0.2 cm^{-1}/GPa in the pressure range from 0 to 8 GPa, then almost zero (a plateau) in the pressure range from 8 GPa to 14 GPa, followed by a smaller value of 3.5 ± 0.2 cm^{-1}/GPa at even higher pressure. It can be clearly seen that the plotted G-band frequency–pressure curve of the SWNT peapod filled with C_{60} shows a similar evolution with that of pristine SWNTs. It is noteworthy that the frequency coefficient of the C_{60}@SWNTs peapod at the first stage of 0–8 GPa is obviously smaller than that of pristine SWNTs (7.8 ± 0.2 cm^{-1}/GPa), which may be caused by the C_{60} filling and the smaller diameters of the pristine SWNTs compared to those of the SWNTs filled with C_{60}. However, the frequency coefficient after the plateau is almost the same as that of pristine SWNTs (3.2 ± 0.2 cm^{-1}/GPa), and both are close to that of the G-mode frequency variation of graphite under high pressure.

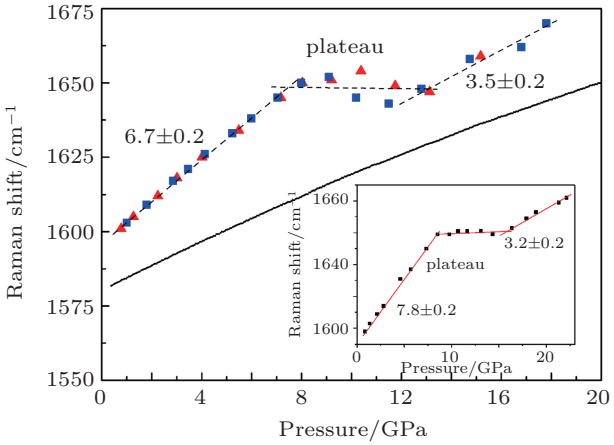


Fig. 4. (color online) Pressure dependence of G-band frequency of peapod sample, obtained with excitation wavelengths of 830 nm (triangle) and 514 nm (square), compared with the data of graphite (black line). Insert is the pressure dependence of G-band frequency of empty SWNTs (excitation wavelength: 830 nm).

The curves for the RBM frequency of SWNTs with or without C_{60} filling as a function of pressure are linear throughout the plateau stage of G-band (Fig. 3(a)). The slopes before and after the C_{60} filling are about the same, 6.5 cm^{-1}/GPa, indicating that the C_{60} filling has little effect on the radial modes of SWNTs under pressure. The blue shift in RBM of C_{60}@SWNTs may be caused by the increased interaction between SWNT and C_{60}.

Let us now turn to discuss the structural evolution of SWNTs filled with C_{60} under high pressure. For the C_{70}@SWNTs peapod, it was found that FWHM of RBM (diameter similar to this work) changes suddenly with pressure at 2 GPa,[14] which was explained by the cross section change of SWNT from circle to ellipse shape. With pressure increased to 10–15 GPa, a plateau was also observed in the curve of the G-band frequency versus pressure, which was interpreted by the collapse of the SWNTs. In our experiment, for

the C_{60}@SWNTs peapod samples, it is observed that the frequency and FWHM of RBM increase with pressure, indicating no obvious change of the cross section of SWNT at least below 4.4 GPa, or only a gradual cross section change under pressure, different from the behavior of the C_{70}-peapod sample. As we know, C_{70} can stand or lie in the interior channels of SWNTs. As the pressure increases, SWNTs are squeezed and the standing C_{70} molecules may change to lie in the SWNTs, resulting in less support from the C_{70} molecules, and thus the nanotubes easily deform.[19] In contrast, C_{60} is a highly symmetric spherical molecule, and no arrangement change like that of C_{70} occurs in SWNTs upon compression, so no obvious change is observed in the RBM FWHM below 2 GPa. As the pressure increases, C_{70} molecules change to lie in SWNTs and the supporting effect of C_{70} to the SWNT is similar to that of C_{60} (equivalent short-axis diameter between C_{60} and C_{70}). Further increasing pressure leads to the presence of a G-band plateau in the C_{60}- and C_{70}-peapod, suggesting a similar structural transition of the nanotubes, i.e., structural collapse of SWNTs, forming similar pod-shaped SWNTs as suggested in Ref. [14]. This transformed structure is different from that of the collapsed hollow SWNTs, for which a peanut-like structure is formed due to a serious radial deformation.

At pressure above 14 GPa, the slope of the pressure dependence of G-band frequency is similar to that of graphite, which indicates that the integrated interaction from the intertube interaction, and the interactions between the interior walls and the C_{60} molecules, as well as the interior walls of the deformed SWNTs, is similar to that of layered graphite under high pressure.

4. Conclusion

The structure evolution of C_{60}@SWNTs peapod under high pressure has been studied by Raman spectra and several structure transitions were observed. At around 10 GPa, SWNTs filled with C_{60} have a similar structural transition to that of pristine SWNTs and C_{70}-peapod, and transform to a peanut-like structure. At higher pressure, G-band of the peapod shows similar Raman evolution to that of graphite under pressure, indicating that the interaction between SWNT and C_{60} increases. It should be noted that at low pressure, no obvious change is observed in the RBM FWHM of SWNTs filled with C_{60}, in contrast to the case of compressing C_{70}-peapod, which can be interpreted by the different arrangement of C_{60} in SWNTs compared to that of C_{70} due to the different molecular shapes.

References

[1] Lu X and Zhong W R 2015 *Chin. Phys. Lett.* **32** 96501
[2] Wei L, Xu Z C, Zheng D Q, Zhang W and Zhong W R 2015 *Chin. Phys. Lett.* **32** 076501
[3] Li X, Zhou W M, Liu W H and Wang X L 2015 *Chin. Phys. Lett.* **24** 057102
[4] Ruoff R S and Ruoff A 1991 *Nature* **350** 663
[5] Elliott J A, Sandler J K W, Windle A H, Young R J and Shaffen M S P 2004 *Phys. Rev. Lett.* **92** 095501
[6] Tang J, Qin L C, Sasaki T, Yudasaka M, Matsushita A and Lijima S 2000 *Phys. Rev. Lett.* **85** 1887
[7] Ni B, Sinnott S B, Mikulski P T and Harrison J A 2002 *Phys. Rev. Lett.* **88** 205505
[8] Zou Y G, Liu B B, Yao M G, Hou Y Y, Wang L, Yu S D, Wang P, Li B, Zou B, Cui T and Zou G T 2007 *Phys. Rev. B* **76** 195417
[9] Kawasaki S, Hara T, Yokomae T, Okino F, Touhara H, Karaura H, Watanuki T and Ohishi Y 2006 *Phys. Lett.* **418** 260
[10] Zou Y G, Liu B B, Wang LC, Liu D D, Yu S D, Wang P, Wang T Y, Yao M G, Li Q J, Zou B, Cui T, Zou G T, WagbergT, Sundqvist B and Mao H K 2009 *Proc. Natl. Acad. Sci. USA* **106** 22135
[11] YaoM G, Wang Z G, Liu B B, Zou Y G, Yu S D, Lin W, Hou Y Y, Pan S F, Jin M X, Zou B, Cui T, Zou G T and Sundqvist B 2008 *Phys. Rev. B* **78** 205411
[12] SanMiguel A, Caillier C, Machon D, Barros E B, Aguiar A L and Souza Filho A G 2010 *Crystallography at High Pressure* **435** 446
[13] Alvarez L, Bantignies J L, Le Parc R, Aznar R, Sauvajol J L, Merlen A, Machon D and San Miguel A 2010 *Phys Rev. B* **82** 205403
[14] Caillier Ch, Machon D and San-Miguel A 2008 *Phys Rev. B* **77** 125418
[15] Zou Y G, Liu B B, Yao M G, Hou Y Y, Wang L, Yu S D, Wang P, Cui T, Zou G T, Sundqvist B, Wang G R and Liu Y C 2007 *Acta Phys. Sin.* **56** 5172 (in Chinese)
[16] Yao M G, Liu B B, Zou Y G, Li D M, Ai X L, Wang L, Yu S D, Zou G T and Sundqvist B 2006 *J. Phys. Chem. B* **110** 15284
[17] Liu X, Pichler T, Knupfer M, Golden M S, Fink J, Kataura H and Achiba Y 2002 *Phys. Rev. B* **66** 045411
[18] Schindler T L and Vohra Y K J 1995 *J. Phys.: Condens. Matter* **7** 637
[19] Guan L H, Li H J, Shi Z J, You L Pand Gu Z N 2005 *Solid State Comm.* **133** 333