Optical properties of fullerenes encapsulated in single-wall nanotubes

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Abstract Single-wall carbon nanotubes (SWNTs) encapsulating specified fullerenes, so called fullerene-peapods, were synthesized in high yield using a sublimation method. High-resolution transmission electron microscopy revealed that almost all nanotubes are filled with high-density fullerene chains. We measured Raman spectra and optical absorption spectra of C_{60}- and C_{70}-peapods to see vibrational properties and electronic structures of peapods. In the case of C_{60}-peapods, Raman intensity of C_{60} modes decreased rapidly by laser irradiation. The final spectrum at room temperature is similar to that of the orthorhombic polymer phase. One-dimensional photopolymerization was strongly suggested. Optical absorption spectrum of fullerene-peas is similar to that of fullerene thin film. A charge transfer exciton band at 2.6 eV was observed in relatively large intensity even in the one-dimensionally aligned fullerenes though each constituent has only two neighbors.

1 Introduction

Single-wall carbon nanotubes (SWNTs) encapsulating fullerenes, what is called fullerene-peapods, are considered to be a new solid phase of carbon constructed by zero- and one-dimensional sp^2 network systems. This new solid should have interesting electronic properties because of the mixed dimensionality. Saito and Okada [1] have calculated the band structure of (10,10) nanotube encapsulating C_{60}, and found some anti-crossings in the flat conduction band, which indicate the considerable interactions between conduction electrons of C_{60} and nanotube. They claimed that fullerene-peapods could be a good candidate for a possible superconductivity by alkaline metal doping. Peapods were first revealed by Smith et al. [2] and then were synthesized in high yield by Burteaux et al.[3]. However, no one succeeded to measure optical properties of peapods to date. Then we tried to make peapods in sufficient yield to measure the optical properties by using a gas phase reaction.

2 Experimental

Carbon soot containing SWNTs were produced by laser furnace technique using Ni/Co catalyst [4]. By considering diameters of fullerenes and van der Waals spacing, the diameter of nanotube should be larger than that of (10,10) to get higher yield of encapsulations. Since the diameter distribution of SWNTs can be controlled by the furnace temperature [5], we have got thick SWNT samples by setting the furnace temperature for 1250 °C. To get a high-purity peapod sample, fullerenes co-existing with nanotubes should be removed completely. Fullerene-free SWNTs could be obtained by heating carbon soot at 1250 °C in vacuum without exposure to the air. The soot was refluxed in 15 % H_2O_2 to remove amorphous carbon and then washed in HCl solution to remove metal particles [5,6]. The purity of resulting SWNT material was estimated to be higher than 90 %. Since the purification process removes caps of SWNTs [8], the purified SWNTs are ready to encapsulation of fullerenes. A sheet of SWNT paper was put in a quartz ampoule with fullerene powder. The ampoule was evacuated to high vacuum. Then the sheet was heated up to 600 °C to remove all adsorbed molecules. The sheet and the fullerenes were sealed in the ampoule and were heated in a furnace up to 650 °C. After keeping the temperature for two hours, the ampoule was cooled down to room temperature. The SWNTs paper was sonicated in toluene for 1 hour to remove fullerenes coated on SWNTs surface. The sample was then filtered to get a sheet of peapod paper. In the above procedure, a specific fullerene can be selected. In this work, we used C_{60} and C_{70} in 99 % purity.

3 Results and Discussion

In both cases, C_{60}- and C_{70}-peapod, we have succeeded to synthesize high purity peapod samples. Figure 1 shows typical high-resolution transmission electron microscope (HRTEM) images and an electron diffraction pattern of C_{60}-peapods. Although HRTEM photographs obtained are similar to those shown in the previous work [3], a yield of fullerene encapsulation of our sample is much higher. It is difficult to find empty SWNTs in HRTEM photographs. Furthermore, a cross section image evidently indicates that every nanotube is encapsulating C_{60} molecules even in the case of a thick bundle. By attentive observations, it was found that C_{60} molecules in a large diameter nanotube tends to form zigzag chains. This suggests a formation of dimers. We
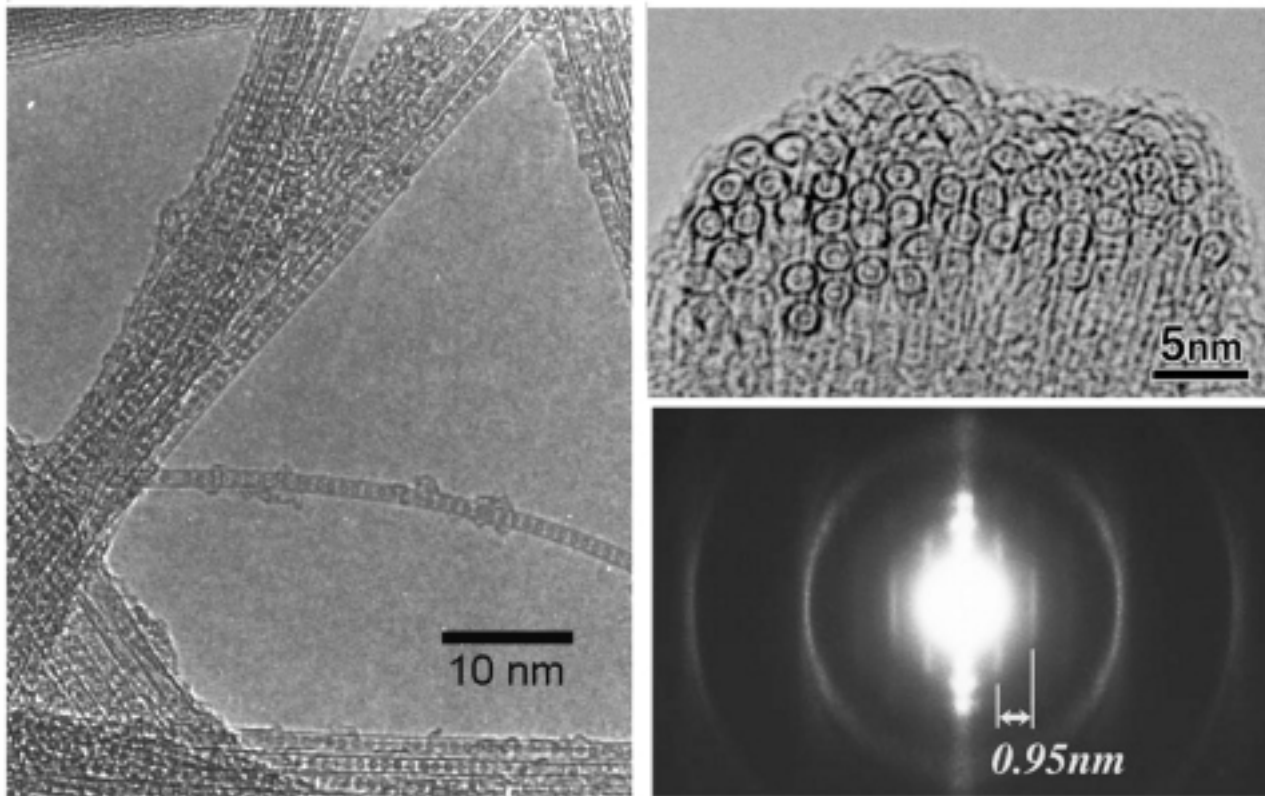
Fig. 1 High-resolution transmission electron microscope images of C_{60}-peapods. The left figure shows a side view of thin bundles and the upper right figure shows cross section image of the bundle. Evidently, C_{60} molecules are observed inside SWNTs in high yield. The right lower figure shows a typical electron diffraction pattern of the peapod bundle. Inter C_{60} distance estimated from streaks is 0.95 nm.

have estimated a filling rate of C_{60}- and C_{70}-peas to be higher than 70 % by HRTEM observations.

By an electron diffraction pattern for a thick bundle, we found new streak lines inside the first arc corresponding to (100) reflection by the graphite layer of SWNT. These streak lines mean one-dimensionally aligned dots; i.e. fullerenes in nanotubes. From the spacing of streaks, we can estimate the inter-ball distances. In the case of C_{60}-peapods, C_{60}-C_{60} distance is estimated to be 0.95 nm. This result is very interesting because the distance obtained is just the intermediate value. In a fcc crystal, C_{60}-C_{60} distance is 1.00 nm while it is 0.92 nm in a polymer crystal [9]. The intermediate distance suggests two possible structures. One of them is a mixture of oligomers and monomers, which may indicate intermediate inter-ball distance as an average. In this case, however, streaks should be broad, which is inconsistent with the observed sharp diffraction streaks. The other possible structure is loosely bonded C_{60} chain due to van der Waals interaction between C_{60} and SWNT. In the case of C_{70}-peapods, we observed double streak lines. The narrower spacing corresponds to 1.10 nm and the wider spacing corresponds 1.00 nm. These values correspond to C_{70}-C_{70} distance of lying C_{70} chain and that of standing C_{70} chain, respectively [9]. This result indicates that C_{70} molecules in SWNT are not rotating

freely. Their long axis is fixed at room temperature similarly to the spinning nature of hcp C_{70} crystal.

Even after washing in toluene, peapod samples gave strong Raman signals from the encapsulated fullerenes. Figure 2 shows typical Raman spectra of C_{60}-, C_{70}-peapods and a C_{70} film. The basic spectrum structure of C_{70}-peapods can be explained by Raman active modes of C_{70} molecules superposed on those of SWNTs. At sight, however, it is found that there are some anomalies in relative Raman intensity and peak widths. Raman mode intensity lying higher that 1100 cm^{-1} is strongly reduced. For example, an intensity ratio between peaks at 1229 and 702 cm^{-1} in C_{70} film is 5 times larger than that in C_{70}-peapods. Similarly, the intensity ratio between peaks at 1469 and 1445 cm^{-1} is reversed. Further, most of peaks show appreciable broadening. These anomalies are probably caused by van der Waals interaction between C_{70} molecules and SWNTs.

In the case of C_{70}-peapod we did not observe any phenomenon concerning with a photopolymerization. Thus we can try to estimate a filling rate of C_{70} molecules in SWNTs. If we use a peak at 702 cm^{-1}, the intensity in C_{70}-peapod is 1/2 of that in C_{70} film. We have to consider the difference in molecular density between hcp C_{70} crystal and full filled C_{70}-peapods, as well as a strong optical absorption by surrounding SWNTs.
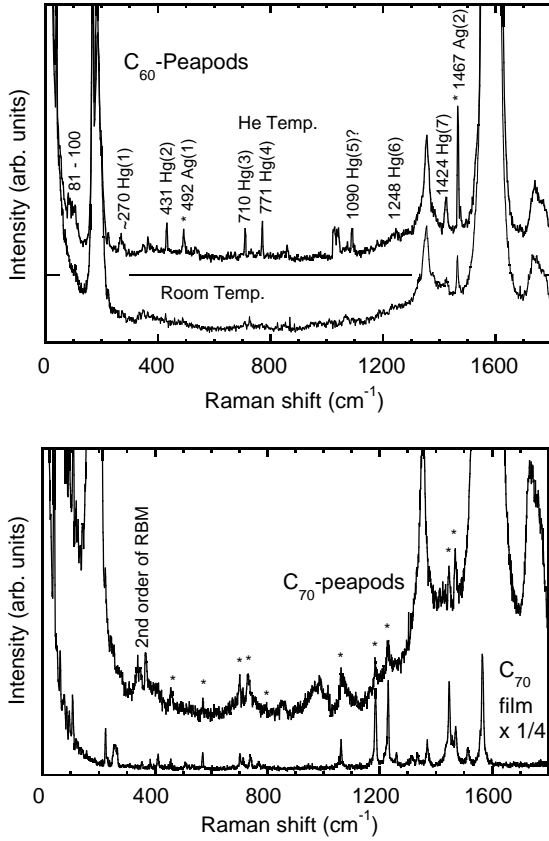
Fig. 2 Raman spectra of C_{60}- and C_{70}-peapods. The upper figure shows Raman spectra of C_{60}-peapods at liquid-helium and room temperature. The lower figure shows the Raman spectra of C_{70}-peapods and C_{70} film measured under the same condition at room temperature. Laser wavelength is 488 nm.

Fig. 3 Optical absorption spectra of C_{60}- and C_{70}-peapods. The upper figure shows optical absorption spectra of C_{60}-peas, thin film and hexane solution measured at room temperature. The lower figure shows the C_{70}-peas. Absorptions by empty SWNTs are subtracted for eyes.

These factors are depending on the morphology of nanotubes that is not well known and also depending on how many kinds of nanotubes are coexisting in the sample. In other words, Raman intensity of C_{70}-peas is depending on a number of nanotubes that are not resonated with the excitation laser. It is difficult to estimate these factors but a filling rate of C_{70} in our sample can be simply estimated to be 50 % as a minimum guaranteed value. This is consistent with the filling rate estimated from HRTEM observations.

In the case of C_{60}-peapod, Raman modes corresponding to C_{60} molecules decreased very quickly by laser irradiation at room temperature. Since the final spectrum is similar to that of orthorhombic polymer crystal synthesized under high pressure and high temperature [10], one-dimensional photopolymerization was suggested. To see the unpolymerized state, it should be necessary to measure the Raman spectrum at low temperature where the spinning of C_{60} is stopped. The sample was annealed and cooled down to liquid helium temperature without exposure to light. Then the Raman spectrum did not show any change by the irradiation of laser. All the Raman active modes of C_{60} molecule were observed. Fur-
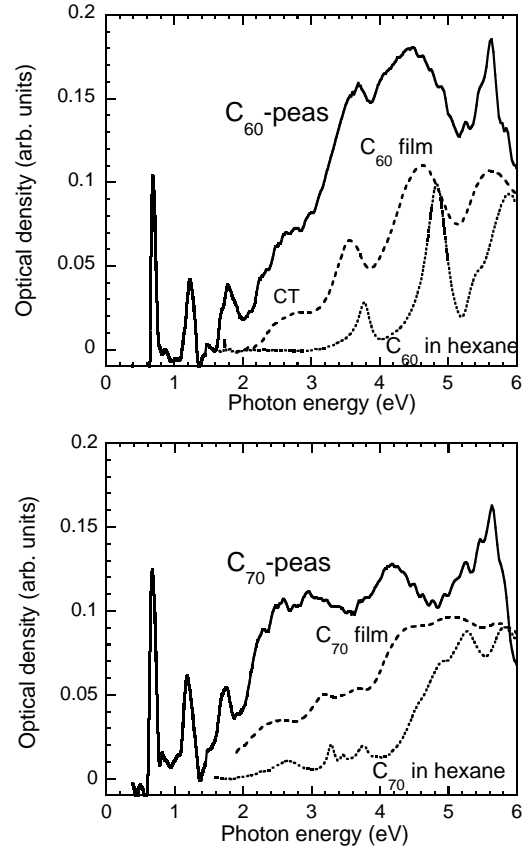
ther, additional peaks were observed around 90 cm^{-1} that is close to an external vibrational mode of C_{60} dimer at 96cm^{-1} [11]. Although the frequency is slightly lower than the intrinsic dimer mode, the peak should be the external vibrational modes of the dimers or the oligomers inside nanotubes. The most distinctive feature of the spectrum is very weak Ag modes. Peak frequencies of Ag modes are lower than the intrinsic ones and are the same value to the orthorhombic polymer phase. The significant reduction of Ag modes intensity and low frequency external modes suggest a formation of the dimers or oligomers. However, it is well known that Hg(1) and Ag(1) modes are sensitive to the formation of the dimer. In the case of C_{60} dimer phase, Hg(1) and Ag(1) modes split into three peaks [11]. In the case of peapods, a broadening of Hg(1) mode was observed but no splitting of the other modes were observed. Further, it is apparent that C_{60} molecules are not polymerized at liquid helium temperature. These antinomic results lead to the intermediate states of C_{60} molecules that are loosely bonded together under van der Waals interactions between C_{60} and nanotubes because the results cannot be explained only by interactions between C_{60} molecules. This condition is consistent with the result of electron diffraction.

Finally, we think about the spinning nature of C_{60}-peas. Since the 2+2 cycloaddition reaction is depending on the meeting probability of a pair of double bonds, photopolymerization concerns with the spinning nature of C_{60}s. Since the temperature dependence of photopolymerization of C_{60}-peas is similar to the fcc crystalline phase, the spinning nature of C_{60}-peas should be also similar to the crystalline phase.

Optical absorption spectra of peapods are indicated in Fig. 3. Where, optical absorption by empty SWNTs was subtracted for convenience. Sharp three peaks at 0.7, 1.2 and 1.8 eV are residuals of absorption peaks of SWNTs, which are corresponding to the optical transition between spikes due to one-dimensional van Hove singularities [12]. The lowest two peaks are corresponding to semiconducting nanotubes and the third lowest peak is corresponding to metallic ones in the sample [13]. Broadening and up-shift of absorption peaks by encapsulation of fullerenes causes these residuals. It is found that effects of encapsulation on electronic structure of nanotubes are similar for both the semiconducting and metallic nanotubes. On the other hand, structures from 2 to 5 eV are mainly ruled by fullerenes. At sight, it is found that the absorption spectrum of C_{60}-peas is similar to that of thin film more than isolated molecules in hexane. The bandwidth of each peak is broader than those in the thin film. We can observe similar band broadening in a photopolymerized C_{60} thin film. On the other hand, in both C_{60}- and C_{70}-peas cases, absorption bands show downshifts compared with those in the thin film. The downshifts of absorption bands between the isolated molecules and thin films are thought to be explained by dipole interactions [14]. In other words, differences in local field cause peak shifts. Since the local field correction is strongly depending on the symmetry, the downshifts observed fullerene-peas are probably caused by differences in local field in SWNT.

Absorption band at 2.6 eV in thin film is usually assigned as an absorption by charge transfer (CT) excitons [9,14]. The CT exciton band is observed in C_{60}-peas with similar relative intensity to the thin film. If the charge transfer occurs between C_{60} molecules, intensity of CT exciton band should depend on the number of neighbors. C_{60} in fcc crystal has twelve neighbors, while C_{60}-pea has only two neighbors in the nanotube. By considering the difference in number of neighbors, the relative absorption intensity of CT excitons in C_{60}-peapod should be anomalously large. If the anomaly is caused by the interactions between C_{60} and nanotubes, similar anomaly should be observed in C_{70}-peas. Furthermore, if C_{70}s are standing in a nanotube that was confirmed by the electron diffraction, the interaction between C_{70}s and the nanotube should be larger than that in the C_{60}-peapod. Indeed, in the case of C_{70}-peapod, very large absorption band around 2.6 eV is observed.

4 Summary

In the case of C_{60}-peapod, results of electron diffraction, Raman scattering and optical absorption lead to a similar image, a formation of dimers or oligomers as an initial state. However, detailed structure is not clear. A kind of charge transfer between C_{60} and SWNT should play an important role to characterize the vibrational and the electronic properties of C_{60}-peapods. In the case of C_{70}-peapods, such intermediate polymer phase was not suggested. However, interactions between C_{70} peas and SWNT are stronger than C_{60}-peapods.

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