

Optical Properties of Fullerene-Peapods

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Abstract. Single-wall carbon nanotubes (SWNTs) encapsulating fullerenes, so-called fullerene-peapods, were synthesized in high yield. High-resolution transmission electron microscopy revealed that almost all nanotubes are filled with high-density fullerene chains. We measured Raman spectra of C₆₀- and C₇₀-peapods. In the case of C₆₀-peapods, C₆₀ Raman active mode intensity decreased rapidly by laser irradiation at room temperature. The final spectrum is similar to that of orthorhombic polymer phase, which indicates one-dimensional photopolymerization. At liquid helium temperature, no photopolymerization was observed, and the Raman spectra obtained indicates a feature of C₆₀-dimer phase. Furthermore, C₆₀-C₆₀ distance estimated from electron diffraction pattern measured at room temperature is consistent with C₆₀-dimer phase. The spontaneous dimerization should be explained in part by internal high-pressure effect.

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 sp² network systems (1,2). Since, in general, a physical property of solid is strongly depending on its network dimensionality, fullerene-peapods should have interesting properties due to the mixed dimensionality. Saito and Okada (3) have calculated the band structure of (10,10) nanotube encapsulating C₆₀, and found an anti-crossing between a flat conduction band of C₆₀ and a linear band of nanotube, which indicates a considerable interaction between conduction electrons with different network dimensionality. In this work, we successfully synthesized high-yield peapod samples and measured Raman spectra of C₆₀- and C₇₀-peapods.

EXPERIMENTAL

By considering a diameter of C₆₀ and van der Waals spacing, the best diameter of nanotube for fullerene encapsulation is that of (10,10). To get higher yield of encapsulations, it is desired to control diameter distribution of SWNTs to be thicker than (10,10). Laser furnace technique realizes a diameter control by changing catalysts and a furnace temperature (4). We chose NiCo (5) as a catalyst and we got thick enough SWNT samples by setting the furnace temperature to 1250 °C. Typical

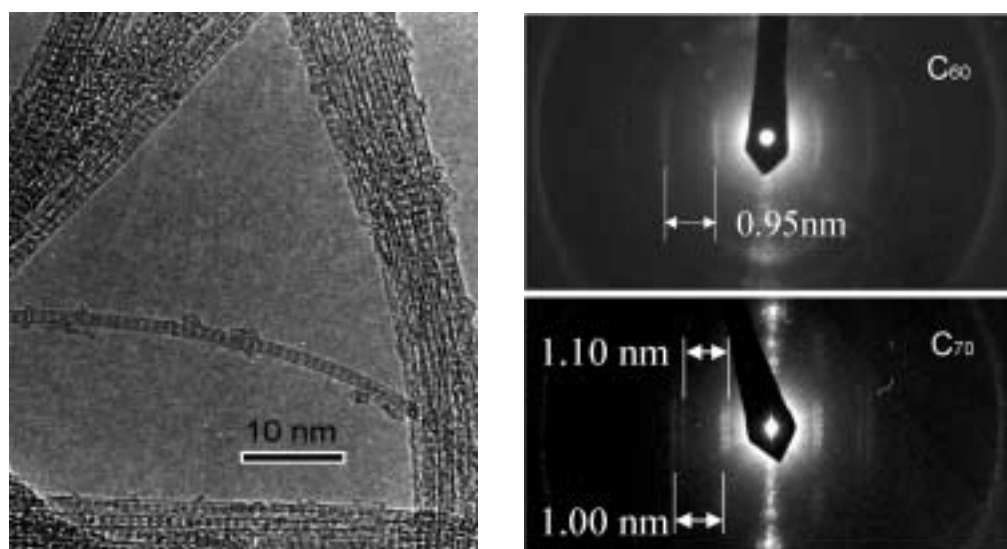


FIGURE 1. Typical HRTEM image of C₆₀-peapods (left photograph) and electron diffraction patterns of C₆₀- (upper right) and C₇₀-peapods (lower right). Inter fullerene distances were estimated from streaks originating from fullerenes one-dimensionally aligned inside nanotubes.

diameter of the sample is estimated to be 1.36 nm by X-ray diffraction. To get a high-purity peapod sample, unknown fullerenes co-produced with nanotubes are the most undesirable impurities. Fullerene-free SWNTs were obtained by in-situ heating soot at 1250 °C in vacuum. The soot was refluxed in 15 % H₂O₂ water solution at 100 °C to remove amorphous carbon and then washed in HCl solution to remove metal particles (6,7). The purity of resulting SWNT material was estimated to be higher than 90 %. Since purification processes remove 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 and the ampoule was evacuated to 1×10^{-6} Torr. After drying process, 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. In this work, we used C₆₀ and C₇₀ in 99 % purity as fullerene sources.

RESULTS AND DISCUSSION

High purity peapod samples were successfully synthesized in both cases, C₆₀ and C₇₀. Figure 1 shows typical high-resolution transmission electron microscope (HRTEM) images and electron diffraction patterns of C₆₀- and C₇₀-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 C₆₀ molecules even in case of thick bundles. We have estimated a filling rate of C₆₀- and C₇₀-peas to be higher than 70 % by HRTEM observations.

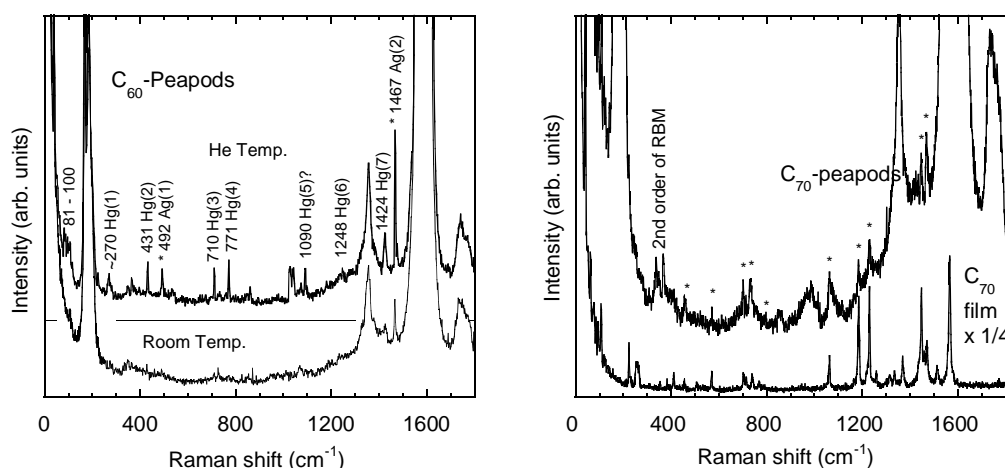


FIGURE 2. Raman spectra of C₆₀- and C₇₀-peapods. The left figure shows Raman spectra of C₆₀-peapods at liquid-helium (upper) and room temperature (lower). The right figure shows the Raman spectra of C₇₀-peapods and C₇₀ thin film measured under the same condition at room temperature. Laser wavelength used is 488 nm.

New streak lines inside the first arc reflection were observed in electron diffraction patterns for peapod-bundles. These streaks mean one-dimensional fullerene crystals in nanotubes. C₆₀-C₆₀ distance was estimated to be 0.95 nm, which is larger than a polymer's value, 0.92 nm, and smaller than a monomer's value, 1.00 nm (9). The intermediate C₆₀-C₆₀ distance suggests a dimer phase as a possible structure of the one-dimensional C₆₀-crystal in nanotube. In case of C₇₀-peapods, we observed very sharp double streaks. The narrower streaks indicate C₇₀-C₇₀ distance to be 1.10 nm and the wider streaks 1.00 nm. The double streaks mean two different crystal structures inside nanotubes, standing and lying alignment (9). Interestingly, there is no intermediate state. This result indicates C₇₀ prefers standing alignment as high-density packing, if the diameter of nanotube is sufficiently large. This may cause larger interaction between C₇₀-peas and nanotubes than C₆₀-peapods.

Figure 2 shows typical Raman spectra of C₆₀-, C₇₀-peapods and a C₇₀ film. In the case of C₆₀-peapod, A_g(2) Raman modes of C₆₀ molecule decreased very quickly by laser irradiation at room temperature. Since the final spectrum is similar to that of orthorhombic polymer (10), formations of one-dimensional photopolymers were suggested. An unpolymerized Raman spectrum was measured at liquid helium temperature. Where, all the Raman active modes of C₆₀ molecule were observed. Further, additional peaks were observed around 90 cm⁻¹ that is close to an external vibrational mode of C₆₀ dimer at 96cm⁻¹ (11). Although the frequency is slightly lower than the intrinsic dimer mode, the peak should be originating from dimers inside nanotubes because of the following reasons. The most distinctive feature of the spectrum is very weak A_g modes. Peak frequencies of A_g modes are lower than the intrinsic ones and are the same value to the orthorhombic polymer phase. It is well known that H_g(1) mode is sensitive to a formation of dimer (11). A broadening of H_g(1) mode observed is consistent with the dimerization. The significant reduction of A_g modes intensity and a appearing of low frequency modes strongly suggest a formation of dimers.

In the case of C₇₀-peapods, all the Raman active modes of C₇₀ were observed even at room temperature and no photoreaction was observed. At sight, however, it is found that there are some anomalies in relative Raman intensity and peak widths. Raman mode intensity lying higher than 1100 cm⁻¹ is strongly reduced. For example, an intensity ratio between peaks at 1229 and 702 cm⁻¹ in C₇₀ film is 5 times larger than that in C₇₀-peapods. Further, most of peaks show appreciable broadening. These anomalies are probably caused by anisotropic interactions between C₇₀s and SWNTs. If we use a peak at 702 cm⁻¹ as a standard, however, we can estimate a filling rate of C₇₀ to be higher than 50% by using mode intensities of the peapod and the thin film.

A spontaneous dimerization and high-density packing of C₇₀ are probably caused in part by an internal high-pressure state. A fullerene molecule at a tip of nanotube pushes fullerenes inside driven by a van der Waals interaction. Tománek has calculated an internal pressure to be 0.1 GPa caused by this effect (12). The high-pressure state stabilizes a dimer phase (13) and standing C₇₀s at room temperature. This effect is very interesting for future applications of peapod materials as pressurized nano-cylinders.

ACKNOWLEDGEMENTS

Authors thank Prof. Susumu Saito, Prof. Okada and Prof. Tománek for fruitful discussions about peapod materials. Authors thank Mr. Misaki for electron diffraction measurements. This work was supported in part by Japan Society for Promotion of Science, Research for the Future Program and supported in part by the Grant-in-Aid for Scientific Research on the Priority Area "Fullerenes and Nanotubes" by the Ministry of Education, Science, and Culture of Japan.

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