Fullerene-peapods: synthesis, structure, and Raman spectroscopy

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Abstract. Single-wall carbon nanotubes (SWNTs) encapsulating fullerenes, so-called fullerene-peapods, were synthesized in high yield by using diameter-selected nanotubes as pods. High-resolution transmission electron microscopy revealed high-density fullerene chains inside nanotubes. X-ray diffraction measurements indicate 60% filling of C_{60} molecules in a macroscopic average. Room temperature Raman spectra show one-dimensional photopolymerization of C_{60} inside nanotubes by blue laser irradiation, indicating molecular rotation inside. In C_{70}-peapod case, Raman active modes peculiar to C_{70} were strongly suppressed by encapsulation. The suppression is probably caused by deformation of molecule due to the unisotropic interaction between C_{70} and SWNT. Anomalous resonance effects in C_{70}-peas suggest hybridization of electronic states of C_{70} and nanotubes. High-symmetry mode Raman intensity suggests the filling factor to be higher than 50%, which is consistent with the X ray diffraction analysis.

INTRODUCTION

Single-wall carbon nanotubes (SWNTs) have large internal space where molecules can be introduced by de-capping. Fullerenes are most favorable molecules for encapsulation because of their fit diameters. Generally, physical properties of solids are strongly depending on a network dimensionality. Since fullerene-peapods have mixed network dimensionality, it is expected they should have very interesting physical properties. Indeed, Okada (1) has indicated the very attractive band structure in C_{60}@(10,10), where the LUMO band of C_{60} goes down to Fermi level of (10,10) linear band and thus the system has two kinds of one-dimensional carriers from nanotube and C_{60}. Okada suggested that the Piels instability might induce a kind of dimerization which was often observed in TEM pictures.

Previously, Smith *et al.* (2) have shown very beautiful TEM photographs of fullerene-peapods, but no one could show its electronic properties to date. Difficulties in experiments were probably due to a low yield of encapsulation. At least, we know that commercial NT@rice and HiPco materials are high-purity but are too thin to encapsulate fullerenes. In this work, we used diameter-selected SWNTs and fullerene
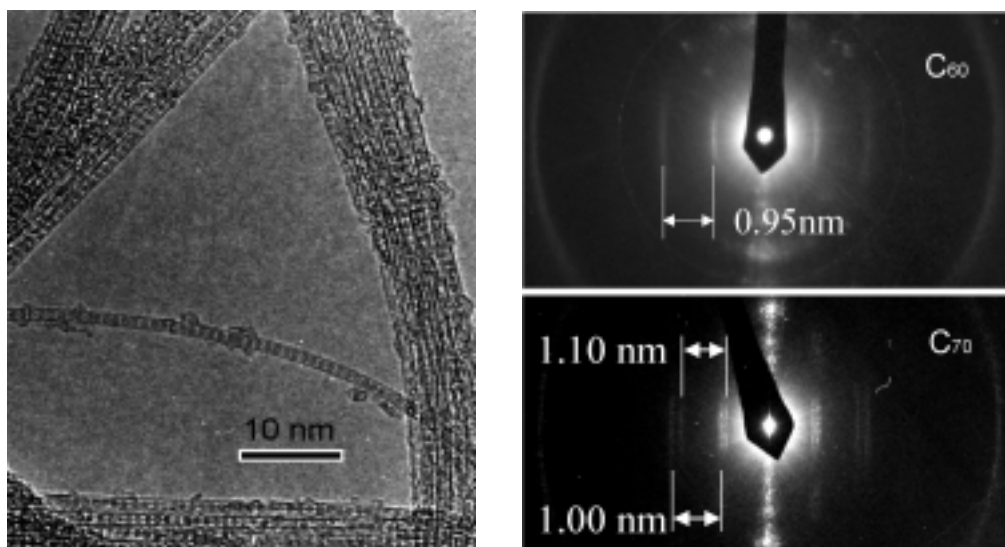
FIGURE 1. Typical HRTEM image of C_{60}-peapods (left photograph) and electron diffraction patterns of C_{60}- (upper right) and C_{70}-peapods (lower right). Inter fullerene distances were indicated in figure estimated from streaks.

vapor to get high-yield fullerene-peapods. We will show Raman spectra of fullerene-peapods.

EXPERIMENTAL

By considering van der Waals spacing, the best diameter of nanotube for fullerene encapsulation is that of (10,10), 1.36 nm. To get higher yield of fullerene encapsulation, we prepared empty SWNTs applying diameter control technique in the laser ablation method (3). In this method, diameter distribution of SWNTs can be controlled by a sort of catalysts and a furnace temperature. When we choose NiCo alloy (4) as a catalyst and set the furnace temperature to 1250 °C, we can get high-purity SWNTs having mean diameter at 1.36 nm. The diameter distribution was confirmed by the X-ray diffraction (XRD) analysis.

NiCo-carbon composite target can co-produce fullerenes in 10% fraction of raw soot. For the peapods production, unknown fullerenes are the most undesirable impurities. To get fullerene-free SWNTs, soot was heated in vacuum up to 1250 °C and all fullerenes were removed. Then the fullerene-free soot was refluxed in 15 % H_2O_2 water solution at 100 °C for three hours to remove amorphous carbon particles (5,6). Since the soot still contains metal particles, it was washed in HCl solution to remove them. Finally, the purified SWNTs were formed to thin black paper and then dried in vacuum at 650 °C. The purity of resulting SWNT material was estimated to be higher than 90 % by TEM observation. Since the oxidation treatment destroys caps of SWNTs (7) and HCl treatment increases defects on the wall, the purified SWNTs already have sufficient number of entrances for fullerenes.

A SWNT paper was put in a quartz ampoule with fullerene powder and the ampoule was evacuated to 1×10^{-6} Torr. After drying process, fullerene powder was
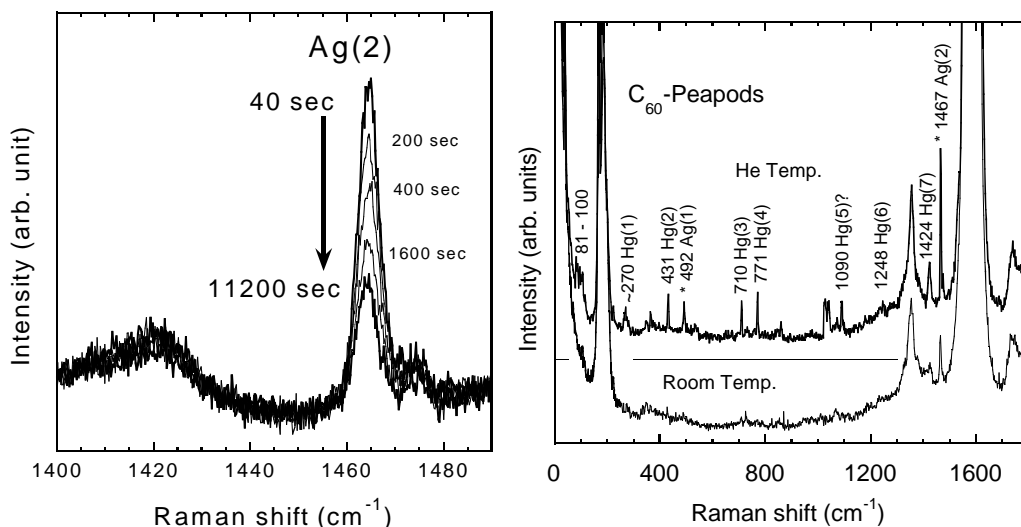
FIGURE 2. Raman spectra of C_{60}-peapods. The left figure shows time resolved Ag(2) mode spectra of C_{60}-peapods at room temperature measured in air. The right figure shows Raman spectrum at liquid-helium (upper) and room temperature (lower). Laser wavelength used is 488 nm.

evaporated and made a film on the SWNT paper. The ampoule was sealed and heated in a furnace up to 650 °C. After keeping the temperature for two hours, the ampoule was cooled down to room temperature. The SWNT paper was sonicated in toluene for 1 hour to remove fullerenes coated on SWNTs surface. After filtration, we got a sheet of peapod paper. Before the optical measurements, the peapod paper was heated in vacuum up to 450 °C to remove toluene. In this work, we used C_{60} and C_{70} powder in 99 % purity as fullerene sources.

RESULTS AND DISCUSSION

The most direct technique to see the fullerene encapsulation is high-resolution (HR) TEM. Figure 1 shows a typical example of HRTEM image of C_{60}-peapods. Results for C_{70}-peapods are not indicated but were very similar. In the electron diffraction pattern, we can observe very clear streaks originating from one-dimensional C_{60} and C_{70}-crystals inside nanotubes. It is very difficult to estimate macroscopic fullerene filling rate from HRTEM results, but we know (10) peak observed in XRD is very sensitive to the molecular encapsulation since the additional electron density inside SWNT changes the form factor (7). We have observed very strong reduction in (10) peak intensity in C_{60}-peapods (8). Careful analysis reveals a filling factor of C_{60} is higher than 60%, which is consistent with the filling factor estimated from EELS measurements. From the streaks in electron diffraction, we can get one-dimensional lattice constant 0.95 nm for C_{60}-peas. On the other hand, XRD indicates 0.97 nm as an average value. We know that the C_{60}-C_{60} distance is 1.00 nm in fcc crystal and 0.92 nm in polymer crystals (9). Intermediate inter-ball distance in one-dimensional C_{60} crystal inside SWNT strongly suggests one-dimensional dimer or origomer phase. On the other hand, in C_{70}-peapods case, double streaks indicate that the sample contains

two kinds of one-dimensional crystals with different lattice constants, 1.00 and 1.10 nm. Each of them just corresponds to the standing eggs and lying egg structure of C_{70}. Interestingly, streaks are very sharp and high-contrast, which means there is no intermediate lattice constants. Indeed, when we used thinner SWNTs as pods, we observed only one streak corresponding to the long lattice constant 1.10 nm. This means C_{70} tend to take a standing alignment if the pod is large enough.

Figure 2 shows typical Raman spectra of C_{60}-peapods. At room temperature, Ag(2) mode of C_{60} molecule was strongly reduced by blue laser irradiation. At helium temperature, on the other hand, we can measure the Raman spectra stably. The temperature dependent photoreaction is very similar to the photopolymerization in fcc C_{60} crystal. Since the photopolymerization is concerned with the spinning nature of C_{60} molecule, this result suggests that C_{60} or C_{60}-origomers are spinning in SWNTs at room temperature. Since the final spectrum is similar to that of orthorhombic polymer (10), laser induced one-dimensional photopolymers were suggested. At helium temperature, all the Raman active modes of C_{60} molecule were observed. Further, additional peaks were observed around 90 cm^{-1} that is close to an external vibrational mode of C_{60} dimer at 96cm^{-1} (11). Additionally, very weak $A_g(1)$ and Ag(2) modes and broadening of $H_g(1)$ mode are indicating formation of dimers or origomers. These results are consistent with electron diffraction and XRD results.

In the case of C_{70}-peapods, all the Raman active modes of C_{70} were observed even at room temperature and no photoreaction was observed. Raman spectra measured by using several laser lines are indicated in Fig. 3. Raman spectra of C_{70}-peas have some anomalies in relative Raman intensity and peak widths. For example, peak intensity at
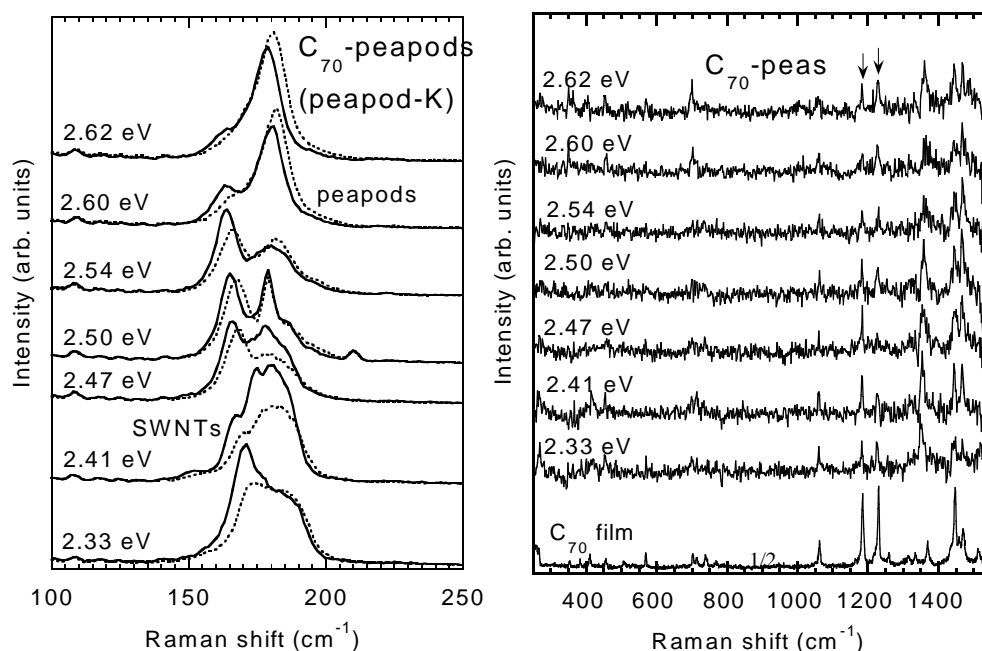

FIGURE 3. Resonance Raman spectra of C_{70}-peapods. Left figure shows radial breathing modes in SWNTs (solid line) and peapods (dashed line). In the right figure, upper seven curves are spectra of C_{70}-peas, I(C_{70}-peapods) – I(SWNTs). The bottom one is that of C_{70} thin film. Excitation laser energies are indicated in figures.

1060 cm^{-1} is a half of that in C_{70} film and independent of excitation energy, showing a filling factor to be higher than 50%. On the other hand, peak intensity at 1184 and 1230 cm^{-1} is strongly depending on the excitation. Intensity ratio I(1060) / I(1184) is anomalously larger than that in C_{70} film and is also depending on the excitation energy. These anomalies should be concerned with the encapsulation. As mentioned above, C_{70}-peapod has two kinds of crystalline structures, standing chain and lying chain. The former structure is permitted only in thick SWNTs. The left figure in Fig. 3 shows that 2.50eV laser can resonate thick SWNTs but 2.62 eV excitation cannot. If the interaction between C_{70} and SWNT depends on the crystal structure, standing or lying, and if electronic states of C_{70} and SWNT are hybridised as predicted in the theoretical calculation (1), resonance effect of C_{70}-peas should reflect electronic structure of wrapping SWNTs. Anomalous resonance effects on C_{70}-peas observed here suggest a considerable hybridisation between C_{70} and SWNT. This is consistent with the optical absorption spectrum of C_{70}-peas that shows large local field effects (12).

If the Dimerization of C_{60} and high-density packing of C_{70}-peas are caused by an internal high-pressure state predicted by Tománek (13), SWNT can be applied to pressurized nano-cylinders in near the future.

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