

Structural Characterization of C₆₀ Nanotubes by Raman and TEM Analyses

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The wall of as-prepared C₆₀ nanotubes contains solvent molecules and the wall structure changes by drying. This change of wall structure was examined by Raman spectrometry. The structural change of C₆₀ nanotubes by heating was also investigated using the Raman and TEM analyses. The C₆₀ nanotubes heated at 300 °C in vacuum turned to a disordered structure with amorphous carbon, and finely dispersed copper nanocrystals were observed by HRTEM, suggesting that copper worked as a catalyst to decompose the C₆₀ nanotubes.

Key words: fullerene nanowhisker, fullerene nanotube, C₆₀, Raman, TEM

1. INTRODUCTION

C₆₀ nanotubes (C₆₀NTs) are single crystalline C₆₀ nanowhiskers (C₆₀NWs) with tubular structure. The C₆₀NTs can be synthesized by the liquid-liquid interfacial precipitation method (LLIP method) combined with ultrasonication, using a pyridine solution saturated with C₆₀ and isopropyl alcohol (IPA).^{1,2,3}

The as-prepared solvated C₆₀NTs have a hexagonal structure with lattice constants $a=1.541$ nm and $c=1.00$ nm.³ before losing solvents by drying, while the C₆₀NTs turn to a face-centered cubic structure with $a=1.424$ nm³, after drying in air. These findings show that the C₆₀NTs can take various crystallographic structures depending on the amount of contained solvent molecules and also suggest that the bonding states of C₆₀ molecules change depending on the change of crystallographic structure. However, detailed analyses on the change of chemical bonding state of C₆₀NTs have not been performed.

On the other hand, Raman spectroscopy is a powerful tool to investigate the chemical bonding states of C₆₀ molecules. Here we show the structural change of C₆₀NTs that are thermally treated in various ways, combining the Raman analysis and the high-resolution transmission electron microscopy (HRTEM) observation.

2. EXPERIMENTAL PROCEDURES

The C₆₀NTs were prepared by the LLIP method combined with ultrasonication, using a pyridine solution with saturated C₆₀ (99.95% pure C₆₀, MTR Ltd., USA) and isopropyl alcohol (IPA).³ The C₆₀-pyridine solution was exposed to UV light (302 nm, UVP Model UVM-57, USA) for 12 h in advance.⁴ The reddish purple color of the solution became red color by this exposure.

A high purity dehydrated pyridine (water content < 50 ppm) and a high purity dehydrated isopropyl alcohol (water content < 50 ppm, Wako Pure Chemical Industries, Ltd.) were used. The synthesis was done in a glove box purged with nitrogen. This glove box has a

stainless steel plate whose temperature can be lowered by the attached copper pipe through which an antifreezing solution is circulated by a cooling system. All glassware is set on the steel plate in order to keep the liquid temperature at a constant value.

In the LLIP method, firstly, 1 mL of the C₆₀-pyridine solution was poured into a transparent glass bottle on the steel plate, and 9 mL of isopropyl alcohol was gently added to the C₆₀-pyridine solution to form a liquid-liquid interface. The glass bottle was kept on the steel plate at about 5 °C for a few days to grow C₆₀NTs.

The C₆₀NTs were observed by a HRTEM (JEOL, JEM-4010, 400kV) and a microscopic Raman spectrophotometer (JASCO, NRS-3100, Japan) at a laser excitation wavelength of 532 nm.

In the Raman spectroscopic measurement for the wet C₆₀NTs, the as-grown C₆₀NTs were pipetted on a slide glass and covered by a cover glass in order to keep the wet state of the C₆₀NTs. The heat treatment of C₆₀NTs were done in a vacuum furnace (1×10^{-3} Pa ~ 3×10^{-4} Pa, IVF298W, THERMO RIKO Co., Ltd., Japan) evacuated by a turbo molecular pump (MH071P, PFEIFFER VACUUM, Germany) for 60 min.

The C₆₀NTs pipetted on copper meshes with carbon microgrids (TEM microgrids) were heated in vacuum as well and examined by Raman spectroscopy and HRTEM.

The thermal analysis of the C₆₀NTs was performed in air using a TG-DTA apparatus (TGD-9000, ULVAC, Japan) at a heating rate of 10 °C min⁻¹.

3. RESULTS AND DISCUSSION

Fig.1 shows a glass bottle containing the grown C₆₀NTs. The C₆₀NTs are shown to be grown from the bottom of the glass bottle.

The C₆₀NTs in the glass bottle were pipetted onto a slide glass and observed as shown in Fig.2. The C₆₀NTs exhibit metallic yellowish color and grow to a length of millimeter order or more.

Fig.3 shows a Raman profile of C_{60} NTs dried in air. Since the Raman profile is very similar to that of pristine C_{60} ,⁵ it is found that the C_{60} NTs dried in air are composed of the C_{60} molecules that are loosely bonded via van der Waals bonding force like the case of C_{60} nanowhiskers dried in air.⁶

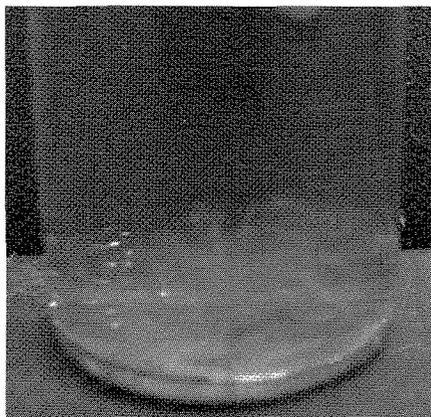


Fig.1 C_{60} nanotubes grown in a glass bottle which was placed on the cooled stainless steel plate.

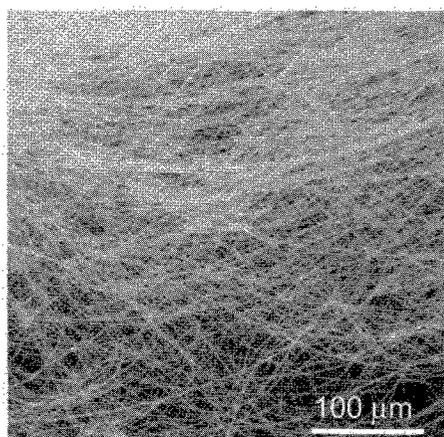


Fig.2 Optical micrograph of the as-grown C_{60} nanotubes.

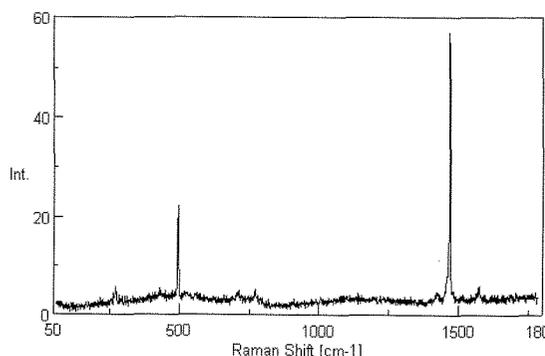


Fig.3 Raman profile of C_{60} nanotubes dried in air at room temperature.

The TG-DTA profile of C_{60} NTs of Fig.4 shows that the decomposition onset temperature (T_0) derived from the differential thermal analysis (DTA) curve is 389 °C in air and is lower than $T_0=428$ °C of pristine C_{60} powder conducted at the same heating rate of 10 °C min^{-1} in air.⁷

The decrease in the TG curve between 100 - 200 °C shows the loss of solvent molecules of about 3 % by heating. This example also suggests that the dried C_{60} NTs have the C_{60} molecules weakly bound via van der Waals bonding force.

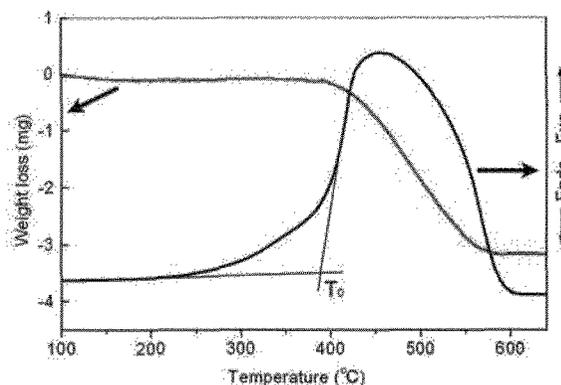


Fig.4 TG-DTA profile for the as-prepared C_{60} nanotubes measured in air.

The change of Raman spectra for the C_{60} NTs heated in vacuum are shown for the $A_g(2)$ peaks in Fig.5. The peak around 1467 cm^{-1} shows non-polymerized C_{60} , while the peaks around 1458 cm^{-1} show polymerized C_{60} .⁸ The peak height of polymerized C_{60} is found to change depending on the annealing temperature. It is seen that the C_{60} NTs retain their structure of C_{60} fullerene cages even heated up to the temperature of 500 °C.

Fig.6 shows the change of averaged peak height ratio I between 1467 cm^{-1} and 1458 cm^{-1} as a function of annealing temperature. It is seen that the I value has the maximum at around 100 °C and the minimum at 300 °C. The C_{60} NTs in the solvent show the smallest ratio, indicating the C_{60} NTs are non-polymerized. The dried sample and the other heat-treated samples show higher peak heights than that of the C_{60} NTs in the solvent. This fact indicates that the C_{60} NTs are polymerized more easily owing to the increase of purity that is caused by the decrease in the contained solvent molecules by the heat treatment. The smaller I values above 300 °C indicate a crystal structure change that is related to the difficulty of polymerization.

The C_{60} nanowhiskers dried in air are apt to be polymerized when a strong laser beam is irradiated on them at room temperature.⁶ However, as shown in Fig.5, the C_{60} NTs dried at room temperature show non-polymerized peak like the case of Fig.3. This fact also indicates that the polymerization is due to the purification of C_{60} NTs that lose the contained solvent molecules by the heat treatment.

In the above experiment, the C_{60} NTs were mounted on slide glasses and heated in vacuum. However, it was found that the C_{60} NTs mounted on a TEM copper mesh with carbon microgrids easily lose their crystalline

structure and turn to amorphous structure as follows.

Fig.7 shows the C_{60} NTs heated on a TEM copper microgrid at 300 °C in vacuum. This figure shows that the C_{60} NTs lost their original crystalline structure and turned to an amorphous structure. The tube walls show a porous structure. This porous structure may exhibit a high specific surface area and be applicable for the platinum catalyst carrier of polymer electrolyte fuel cell electrodes.

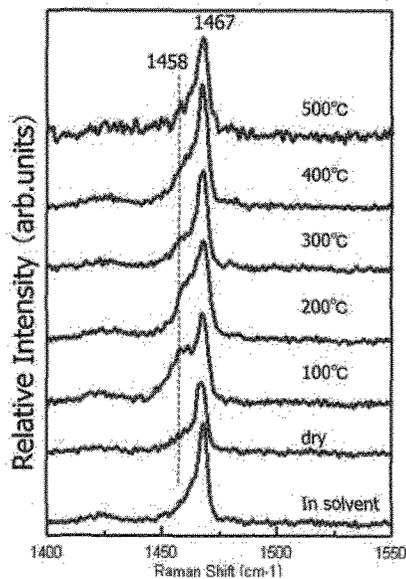


Fig.5 Raman spectra for the C_{60} NTs heated in vacuum.

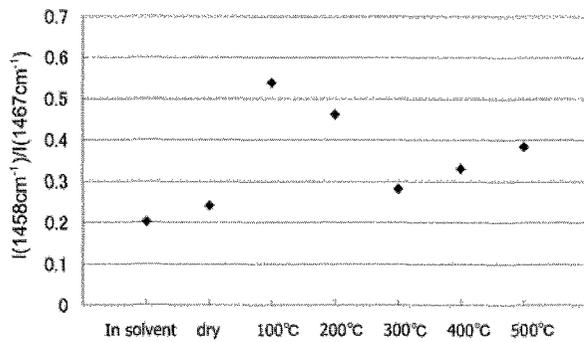


Fig.6 Change of the ratio $I(1458\text{cm}^{-1})/I(1467\text{cm}^{-1})$ as a function of annealing temperature.

A magnified image for a heated C_{60} NT on the TEM mesh is shown in Fig.8. Fine particles with rounded shape are found to be precipitated as marked by rectangle B. As can be seen in Fig.9 of the magnified image for rectangle A, the matrix of the heated C_{60} NT is amorphous.

The precipitate marked by rectangle B of Fig.8 is identified to be copper from Fig.10. The lattice plane spacing corresponds to (111) planes of copper is indicated in the figure. Nanotwins with (111) coherent boundaries are observed. The copper precipitates are surrounded by the amorphous carbon which was formed

by a decomposition of C_{60} . This fact suggests that the copper precipitates worked as the catalysts to decompose C_{60} NTs. This speculation, however, may not be correct since the places without copper precipitates also show the amorphous structure. It is expected that the copper nanoparticles precipitated during cooling. The C_{60} cages must have been destroyed by the copper atoms that uniformly diffused from the TEM copper mesh.

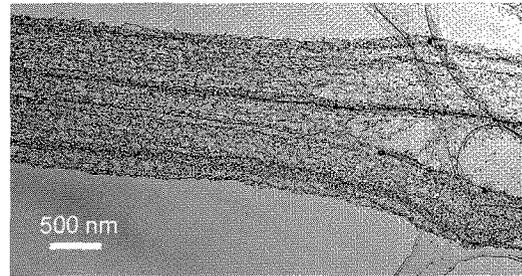


Fig.7 TEM image of the C_{60} nanotubes on a copper mesh heated at 300 °C for 30 min in vacuum.

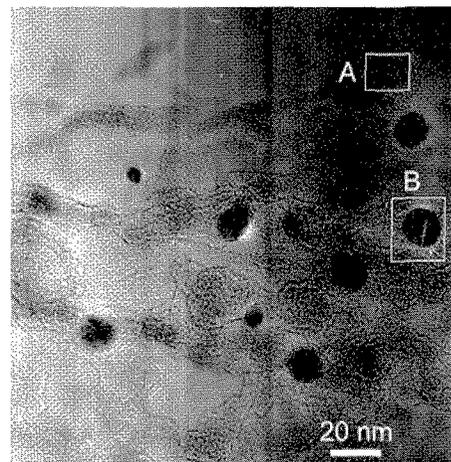


Fig.8 TEM image for a part of C_{60} NT heated in vacuum for 30 min at 300 °C.

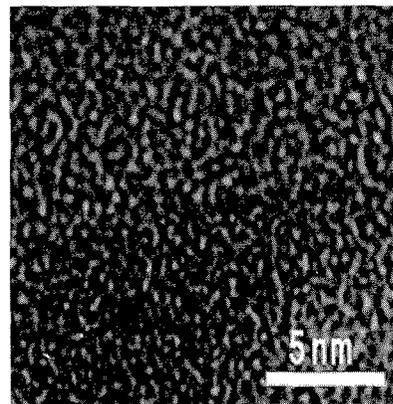


Fig.9 HRTEM image for the part shown by rectangle A of Fig.8.

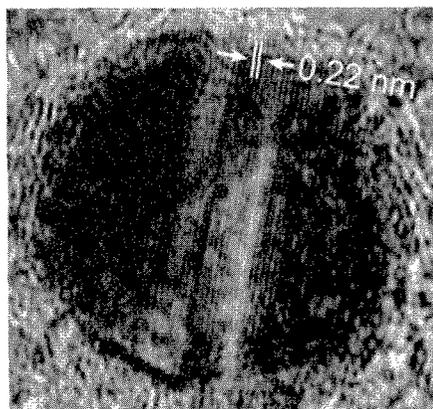


Fig.10 HRTEM image for the precipitate B of Fig.8.

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4. CONCLUSIONS

The present research can be summarized as follows.

(1) The C_{60} NTs dried in air at room temperature showed a Raman profile very similar to that of pristine C_{60} , suggesting that the C_{60} molecules in the dried C_{60} NTs are bonded via weak van der bonding force.

(2) The C_{60} NTs decomposed in air at the onset temperature of 389 °C lower than that of pristine C_{60} .

(3) A strong polymerization of C_{60} NTs was found in the sample heated at 100 °C in vacuum.

(4) The C_{60} NTs heated on a copper mesh were turned amorphous by heating at 300 °C in vacuum and had precipitated copper nanocrystals, suggesting copper worked as a catalyst to decompose the C_{60} NTs.

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