

# TEM and Raman Spectroscopy Analyses of Fullerene Nanowhiskers and Nanotubes

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## ABSTRACT

Crystalline precipitates composed of  $C_{60}$  and  $C_{60}$ (6,7-dimethoxytetralin) were prepared by the liquid-liquid interfacial precipitation method and examined by Raman spectroscopy and transmission electron microscopy (TEM). The as-prepared  $C_{60}$  nanotubes ( $C_{60}$ NTs) dried in air exhibited a Raman spectrum showing a linearly polymerized structure, and a part of them turned to van der Waals polymers after drying in air. On the other hand, the  $C_{60}$ NTs dried in air turned to a polymerized structure by irradiation of UV light. The whiskers prepared by use of  $C_{60}$ (6,7-dimethoxytetralin) showed an  $A_g(2)$  peak of  $1460\text{ cm}^{-1}$  suggesting a polymerization of  $C_{60}$  and a Raman spectrum with sharp and clearly splitted peaks in the range of  $200\text{-}800\text{ cm}^{-1}$ , indicating a good crystallinity.

**Keywords:**  $C_{60}$ , fullerene, fullerene nanowhisker, fullerene nanotube, structure

## 1 INTRODUCTION

Fullerene nanowhiskers (FNWs) are single crystalline fine fibers composed of fullerene molecules like  $C_{60}$  and  $C_{70}$ , and are prepared in solutions by the liquid - liquid interfacial precipitation method (LLIP method) [1,2]. The as-prepared nanowhiskers of  $C_{60}$  and  $C_{70}$  have solvated hexagonal structures which turned to face-centered cubic (FCC) structures through drying in air, losing the contained solvent molecules by evaporation [3]. It is also possible to prepare FNWs with tubular structure and they are called "fullerene nanotubes (FNTs)" [4]. FNWs composed of  $C_{60}$  derivative molecules like  $C_{60}[C(COOC_2H_5)_2]$  ( $C_{60}$  monosubstituted by ethyl ester of malonic acid) can be prepared by the LLIP method as well [5].

Raman spectrometry is a powerful tool to investigate the bonding state of fullerene molecules. This paper shows that the  $C_{60}$ NTs exhibit different profiles depending on their solvated and dried structures and an evidence of

polymerization caused by irradiation of UV light.

And also, it will be shown that a whisker of  $C_{60}$ (6,7-dimethoxytetralin) exhibits a Raman profile with extra peaks that are not observed in pristine  $C_{60}$  and that the extra peaks become clearer than those of a shapeless precipitate of  $C_{60}$ (6,7-dimethoxytetralin), suggesting a better crystallinity of the whisker.

## 2 EXPERIMENTAL

The  $C_{60}$ NTs were prepared using a pyridine solution saturated with  $C_{60}$  (99.5% pure  $C_{60}$ , MTR Ltd., USA) and isopropyl alcohol (IPA) by the LLIP method shown previously [6]. The LLIP method was also applied for a system of toluene solution with saturated  $C_{60}$ (6,7-dimethoxytetralin) and IPA to obtain the precipitates with various morphologies.  $C_{60}$ (6,7-dimethoxytetralin) and  $C_{60}[C(COOC_2H_5)_2]$  used in this research were synthesized at Kyoritsu University of Pharmacy. The dried  $C_{60}$ NTs at room temperature were irradiated by UV light with a wave length of 264 nm (SM-5EC, Bunkoh-Keiki Co., LTD.) for 24 h.

The prepared specimens were investigated by a transmission electron microscopy (JEM-4010, 400kV, JEOL, Japan) and a microscopic Raman spectrophotometer (JASCO, NRS-3100, Japan) at a laser excitation wavelength of 532 nm with a beam intensity of 0.1-1.1 mW and a resolution of  $4.23\text{ cm}^{-1}$ .

## 3 RESULTS AND DISCUSSION

### 3.1 TEM and Raman Spectroscopic Characterization of the Precipitates Prepared from $C_{60}$

A Raman profile for as-prepared  $C_{60}$  nanotubes ( $C_{60}$ NTs) is shown in Figure 1 (a). The spectrum was taken just after pipetting the  $C_{60}$ NTs from the glass bottle. The peaks suggesting one-dimensional polymer of  $C_{60}$  (P) and  $C_{60}$  dimers (D) are indicated, according to ref. [7]. The  $A_g(2)$  peak

of Figure 1 (b) is shifted to  $1459\text{ cm}^{-1}$  and is close to  $1460\text{ cm}^{-1}$  of photopolymerized  $\text{C}_{60}$  [7].

A Raman spectrum of  $\text{C}_{60}\text{NTs}$  dried for 40 days in air is shown in Figure 2 (a), where the peaks indicating one-dimensional polymers (P) and  $\text{C}_{60}$  dimers (D) are observed. The  $\text{A}_g(2)$  peak, however, is splitted into two peaks of  $1458\text{ cm}^{-1}$  and  $1466\text{ cm}^{-1}$  as shown in Figure 2 (b). This result shows that the polymerized  $\text{C}_{60}$  molecules turn to  $\text{C}_{60}$  molecules that are loosely bound via van der Waals bonding force through drying. We showed that the as-prepared  $\text{C}_{60}\text{NTs}$  have a solvated hexagonal structure and turn to a face-centered cubic structure (FCC) with a lattice constant of  $1.424\text{ nm}$  by drying in air [3]. This structural change is consistent with the present bonding change caused by drying.

The hexagonal solvated crystal structure of  $\text{C}_{60}\text{NTs}$  has  $\text{C}_{60}$  molecules that are linearly aligned along the growth axis parallel to the  $c$ -axis of the hexagonal structure [3]. Hence, it is suggested that the as-prepared  $\text{C}_{60}\text{NTs}$  consist of  $\text{C}_{60}$  molecules that are linearly polymerized along the tube growth axis.

On the other hand, the  $\text{C}_{60}\text{NTs}$  dried in air were irradiated by UV light with a wavelength of  $264\text{ nm}$  and observed by TEM as shown in Figure 3.

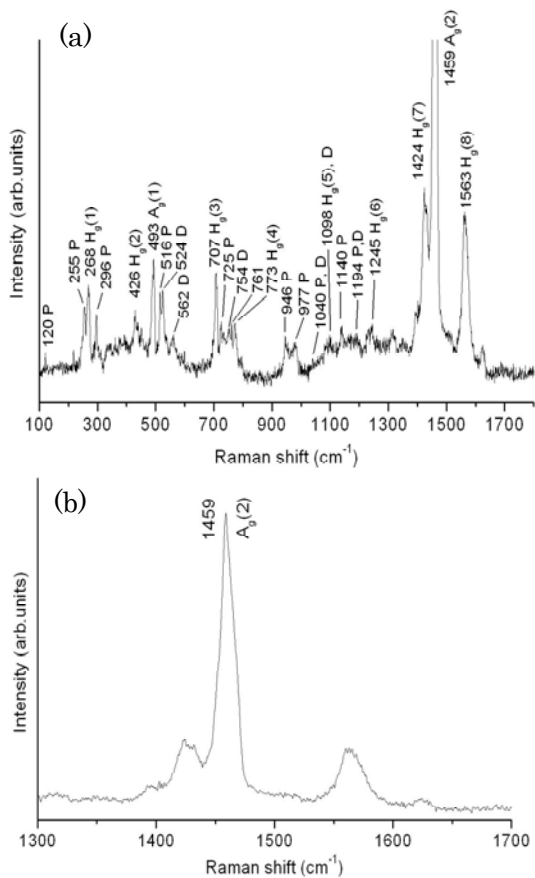


Figure 1 : (a) Raman spectrum for the as-prepared  $\text{C}_{60}\text{NTs}$  and (b) magnified  $\text{A}_g(2)$  profile.

The  $\text{C}_{60}\text{NT}$  irradiated by UV light retains its tubular structure (arrow). The other fine fibers in the figure have diameters of about  $100\text{ nm}$  and have solid structure.

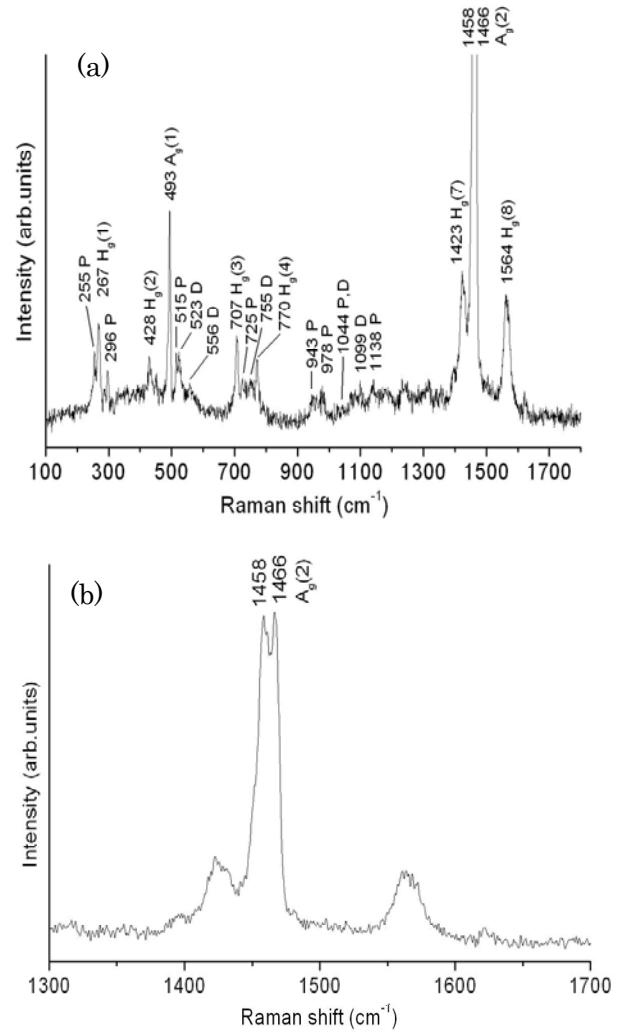


Figure 2 : (a) Raman spectrum for the  $\text{C}_{60}\text{NTs}$  dried in air for 40 days and (b) magnified  $\text{A}_g(2)$  profile.

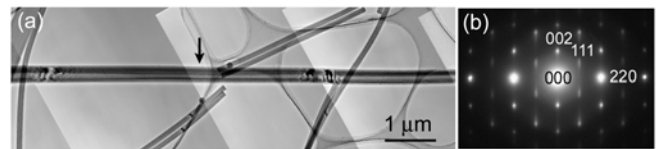


Figure 3 : (a) TEM image for a  $\text{C}_{60}$  nanotube (arrow) irradiated by UV light for 24 h and (b) its SAEDP.

Those solid fibers are the nanowhiskers of  $\text{C}_{60}$ . The tubular structure can be obtained when the whisker diameter is greater than a certain value owing to the finite wall thickness of the whisker [3,4]. The selected area electron diffraction

pattern (SAEDP) for the arrowed  $C_{60}$ NT shows a tetragonal structure like the previous observation for a  $C_{60}$ NT that was dried at room temperature under normal fluorescent room light [6]. The growth axis is parallel to [110] direction along which the  $C_{60}$  molecules are densely packed. The streaked diffraction spots of 111 indicate that high-density planar faults are introduced in the tube wall.

The Raman profile (Figure 4) of the  $C_{60}$ NTs irradiated by the UV light (264 nm) shows a single  $A_g(2)$  peak with a Raman shift of  $1461\text{ cm}^{-1}$ , suggesting a formation of one-dimensionally polymerized  $C_{60}$  along the tube growth axis. The above results show that the  $C_{60}$ NTs change to van der Waals polymers by losing the contained organic solvent molecules, but can be polymerized by the illumination of UV light after drying.

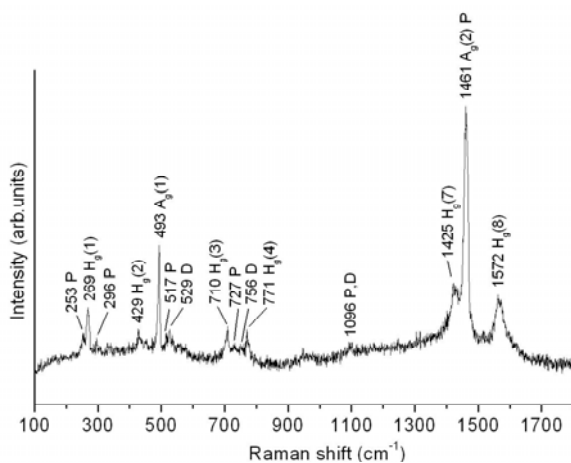


Figure 4 : Raman spectrum for the  $C_{60}$ NTs irradiated by UV light for 24 h.

### 3.2 Raman Spectroscopic Characterization of the Precipitates Prepared from $C_{60}$ Derivative Molecules

As shown in the inset of Figure 5 (a), the whisker of  $C_{60}$ (6,7-dimethoxytetralin) with a diameter of  $1.6\text{ }\mu\text{m}$  and a length of  $9.1\text{ }\mu\text{m}$  was successfully prepared, although it had been thought to be difficult to prepare the whiskers owing to the large side chain of  $C_{60}$ (6,7-dimethoxytetralin) molecule. The  $1460\text{ cm}^{-1}$  peak of  $A_g(2)$  mode coincides with the  $1460\text{ cm}^{-1}$  peak of photopolymerized  $C_{60}$  [8], suggesting that the  $C_{60}$  cages of  $C_{60}$ (6,7-dimethoxytetralin) molecule are one-dimensionally polymerized along the whisker growth axis. A Raman profile of a platy flake of  $C_{60}$  (6,7-dimethoxytetralin) also shows a  $A_g(2)$  peak which is close to the photopolymer of  $C_{60}$  [8](Figure 5(b)). It is to be noted that such peak is between those of the whisker and the pristine  $C_{60}$

powder. Hence, it is suggested that the  $C_{60}$ (6,7-dimethoxytetralin) molecules in the whisker have a more ordered structure than the molecules in the flake. New peaks are found to appear at  $997\text{ cm}^{-1}$  and  $1344\text{ cm}^{-1}$  in Figure 5 (b), and at  $1001\text{ cm}^{-1}$  and  $1323\text{ cm}^{-1}$  in Figure 5 (a). These new peaks are not observed in the photopolymerized  $C_{60}$ [8].

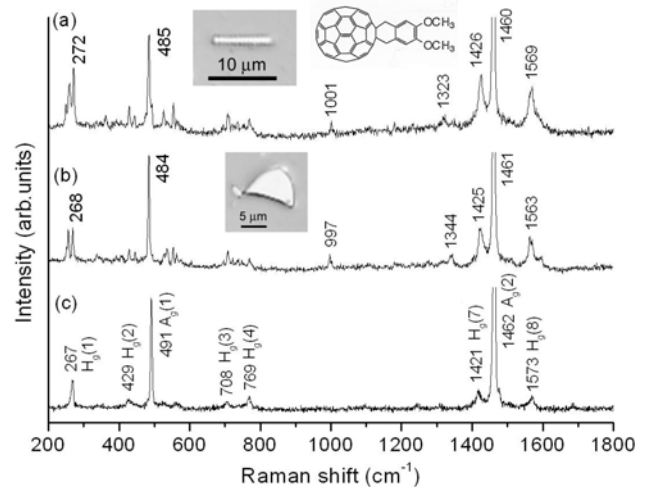


Figure 5 : Raman spectra for (a)  $C_{60}$ (6,7-dimethoxytetralin) whisker (inset) and its structural formula, (b) a platy crystal (inset) of  $C_{60}$ (6,7 - dimethoxytetralin), and (c) pristine  $C_{60}$  powder (99.95%).

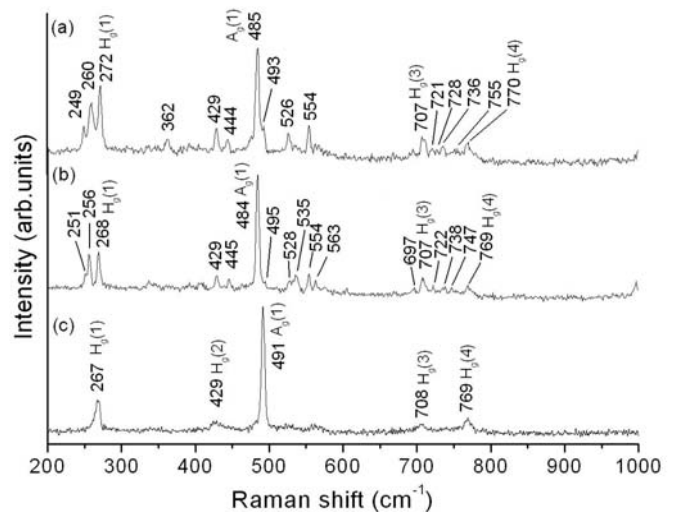


Figure 6 : Replotted Raman spectra in the range of  $200\text{--}1000\text{ cm}^{-1}$  for Figure 5. (a)  $C_{60}$ (6,7-dimethoxytetralin) whisker, (b) platy crystal of  $C_{60}$ (6,7 - dimethoxytetralin), and (c) pristine  $C_{60}$  powder (99.95%).

As shown in Figure 6, the increase in the number of new Raman peaks like the peak at  $362\text{ cm}^{-1}$  as compared with that

of pristine  $C_{60}$  is clear in the Raman shift range of 200 - 600  $cm^{-1}$ . We can see three clearly splitted peaks around the  $H_g(1)$  peak. The peak of 251  $cm^{-1}$  of Figure 6 (b) becomes clearer and appears at 249  $cm^{-1}$  in Figure 6 (a). The extra peaks other than  $H_g(1)$ ,  $A_g(1)$ ,  $H_g(2)$ ,  $H_g(3)$  and  $H_g(4)$  also become clearer in the Raman shift range of 300 - 600  $cm^{-1}$  in Figure 6 (a). The appearance of stronger and clearer peaks suggests that the number of degrees of freedom in the orientation of  $C_{60}$  cages in Figure 6 (a) is smaller than the other cases of Figure 6 (b) and Figure 6 (c) and a better crystallinity of the whisker.

As shown in Figure 7, the Raman spectrum of the shapeless  $C_{60}[C(COOC_2H_5)_2]$  particle shows extra peaks corresponding to one-dimensional  $C_{60}$  polymer (P) and  $C_{60}$  dimers (D) [7]. However, the  $A_g(2)$  peak shows a Raman shift similar to pristine  $C_{60}$ , suggesting a weak bonding between adjoining  $C_{60}$  cages. Although a strong subpeak of  $H_g(1)$  appears at 258  $cm^{-1}$ , the peak of 249  $cm^{-1}$  appearing in Figure 6 (a) is not observed in Figure 7. Hence it is conjectured that the splitting of the  $H_g(1)$  peak is closely related to the linear morphology and good crystallinity of  $C_{60}$  derivative precipitates as shown in Figure 6 (a).

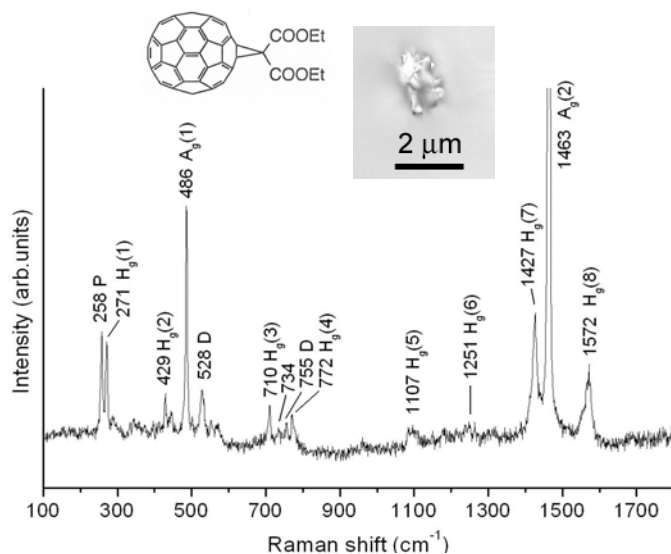


Figure 7 : Raman spectrum for  $C_{60}[C(COOC_2H_5)_2]$  particle (inset). The marks of P and D are “one-dimensional polymer” and “dimer” of  $C_{60}$ , respectively [7].

## 4 CONCLUSIONS

The present research is summarized as follows.

1. The as-prepared  $C_{60}$ NTs showed a Raman spectrum of one-dimensionally polymerized structure, and a part of them turned to van der Waals polymers after drying in air.
2. The  $C_{60}$ NTs dried in air and irradiated by UV light retained their tubular morphology and showed a Raman profile characteristic of one-dimensional polymer of  $C_{60}$ .
3. The  $C_{60}$ (6,7 - dimethoxytetralin) precipitates exhibited clearly splitted  $H_g(1)$  peak, and their  $A_g(1)$  and  $A_g(2)$  peaks significantly shifted to lower wavenumbers.
4. The splitting of  $H_g(1)$  peak of  $C_{60}$ (6,7 - dimethoxytetralin) became clearer in the whisker form, suggesting a formation of linear bonding of  $C_{60}$  cages along the whisker growth axis.
5. It is suggested that the  $H_g(1)$  peak is sensitive to the morphology and crystallinity of  $C_{60}$  precipitates.

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