

## Fabrication of two-component fullerene nanotubes and nanowhiskers by the liquid-liquid interfacial precipitation method

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**Abstract :** Multicomponent fullerene nanofibers (fullerene nanowhiskers and fullerene nanotubes) are expected to exhibit various physical and chemical properties, reflecting those of individual constituent fullerene molecule. As an initial attempt to obtain the multicomponent fullerene nanofibers, two-component fullerene nanofibers composed of  $C_{60}$ ,  $C_{70}$  or  $C_{60}$  derivatives have been successfully obtained by using the liquid-liquid interfacial precipitation method that forms an interface between a fullerene-saturated organic solution and an alcohol. This paper describes the preparation method and the structural characteristics of the two-component fullerene nanofibers.

**Key words :** nanotubes, nanowhiskers,  $C_{60}$ ,  $C_{70}$ , fullerene

### 1. INTRODUCTION

Since the discovery of  $C_{60}$  in 1985<sup>1</sup>, much attention has been paid to fullerenes owing to their unique physical and chemical properties. Preparation of fullerene derivatives has been intensively studied as well. For example, it has been reported that a derivative of  $C_{60}$ ,  $C_{60}>C[PO(OH)_2]_2$ , shows a proton conductivity of  $10^{-2} \text{ Scm}^{-1}$  and is expected to be useful for various electrochemical applications.<sup>2</sup>

On the other hand, the fullerene nanofibers are defined as the thin crystalline solid or tubular fibers that have submicrometer diameters and are composed of fullerene molecules like  $C_{60}$ ,  $C_{70}$  and fullerene derivatives.

The fullerene nanofibers presented in this paper can be prepared by the liquid-liquid interfacial precipitation method (LLIP method)<sup>3</sup> that forms an interface between a fullerene-saturated organic solution (toluene, *m*-xylene or pyridine) and an alcohol (isopropyl alcohol). In the LLIP method, fine fullerene precipitates nucleate at the liquid-liquid interface and grow in the solution to a length on the order of millimeters or more.

The fullerene molecules are usually densely packed along the fiber growth axis, suggesting that direct contacts between adjoining fullerene cages are necessary for the formation of fullerene nanofibers. Although the bonding force between adjoining  $C_{60}$  molecules in the  $C_{60}$  nanowhiskers dried in air has recently been thought as van der Waals force,<sup>4</sup> the detailed whisker formation mechanism has not been clarified except for the fact that the  $C_{60}$  nanowhiskers well grow under illumination of visible light.<sup>4</sup> It has been also reported that the growth rate of  $C_{60}$  nanowhiskers depends on the wavelength of light and significantly promoted by the light with a wavelength between 600 and 675 nm.<sup>5</sup>

The  $C_{60}$  nanowhiskers can be formed into a tubular structure by heat treatment at high temperature in vacuum as well. The tubular nanocarbons were named "fullerene shell tubes", since the shell tubes are formed through evaporation of inside fullerene molecules in the whiskers and the formation of surface thin layers composed of amorphous carbon.<sup>6</sup> The fullerene shell tubes showed a low electrical resistivity of about 0.04  $\Omega\text{cm}$  and a high surface area of about  $400 \text{ m}^2\text{g}^{-1}$ .<sup>7</sup> Since the fullerene shell tubes have inner diameters on the order of 100 nm, various nanosized particles may be incorporated into the inside of the tubes. It is expected that the electrically conductive fullerene shell tubes with a high specific surface area are quite suited for the electrodes of polymer electrolyte fuel cells.

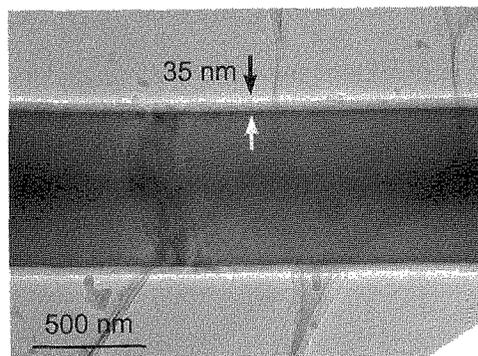


Fig.1 TEM image for a  $C_{60}$  nanowhisker with a core-shell structure.

As shown in Fig.1, one of the morphological characteristics of  $C_{60}$  nanowhiskers is that they have a core-shell structure. The surface layer shell has a

thickness of about 35 nm in Fig.1. It was found that the electrical resistivity of  $C_{60}$  whiskers decreases rapidly with decreasing the whisker diameter.<sup>8</sup> This phenomenon is assumed to be owing to the whisker surface layer with an electrical conductivity much higher than that of the inner part of the whisker. It is considered that the thin surface layer of the whiskers is composed of polymerized fullerene molecules, and hence it is assumed to be difficult for the deeply trapped solvent molecules to escape from the whisker inside owing to the polymerized dense surface layer structure. This may be the reason for the formation of the core-shell structure of fullerene nanowhiskers.

Although the  $C_{60}$  nanowhiskers as shown above exhibit various unique structural and physical properties, multicomponent fullerene nanofibers are expected to exhibit a variety of new properties that reflect the properties of constituent individual fullerene molecule. As an initial attempt, we have investigated the preparation of  $C_{60}$ - $C_{70}$  nanotubes and  $C_{60}$ - $C_{60}$  derivative nanowhiskers. This paper presents the preparation method and their structural characteristics.

## 2. EXPERIMENTAL

The preparation of  $C_{60}$ - $C_{70}$  nanotubes was done as follows. Firstly, a 0.2 mass% pyridine solution of as-received  $C_{60}$ - $C_{70}$  mixed powder (fullerene soot, Tokyo Progress System Ltd., Japan) was prepared. Then, 4 mL of this solution was poured into a transparent glass bottle (9 mL) and then 4 mL of isopropyl alcohol was gently added to the bottle to form a liquid-liquid interface at temperatures of 10°C ~ 20°C under usual fluorescent room light, where the upper phase was isopropyl alcohol and the lower phase was the pyridine solution of fullerene. The glass bottle was capped and allowed to stand at 10°C for two weeks in an incubator.  $C_{70}$  nanotubes were also similarly prepared by using a  $C_{70}$  powder (99.5%, MTR Co., USA). The solid fullerene nanowhiskers were prepared also by the LLIP method using *m*-xylene and pyridine for the solvent of fullerene powders ( $C_{60}$ ,  $C_{60}C_3H_7N$ ,  $C_{60}C(COOH)_2$ ,  $C_{60}[C(COOC_2H_5)_2]$ ) and isopropyl alcohol.

The structure of the precipitates formed in the glass bottles was examined by a high-resolution transmission electron microscope (HRTEM, JEM-4010, 400 kV, JEOL, Japan) and FT-IR (Valor III, Jasco, Japan).

## 3. RESULTS AND DISCUSSION

### 3.1 Precipitates prepared using $C_{60}C_3H_7N$ and $C_{60}C(COOH)_2$

Preparation of fullerene nanowhiskers by using powders with compositions of  $C_{60}C_3H_7N$ -23 mass% $C_{60}C(COOH)_2$  and  $C_{60}C_3H_7N$ -38 mass% $C_{60}C(COOH)_2$  was investigated, where a mixed solvent of *m*-xylene and pyridine (*m*-xylene and pyridine = 1:1) was used for the fullerene solvent. Although most of the precipitates were composed of irregularly shaped crystals with a size of several micrometers, needle-like crystals were also observed to form as shown by

arrows in Figs.2 and 3. These results suggest that two-component  $C_{60}C_3H_7N$ - $C_{60}C(COOH)_2$  whiskers can be obtained by improving the preparation condition. It is considered that the small yield of the  $C_{60}C_3H_7N$ - $C_{60}C(COOH)_2$  whiskers is owing to the fact that direct contacts between adjoining  $C_{60}$  cages along the whisker growth axis were difficult to form. However, as shown in the following examples, it was possible to prepare fine  $C_{60}$  nanowhiskers using a  $C_{60}$  solution containing a high-concentration of  $C_{60}[C(COOC_2H_5)_2]$ .

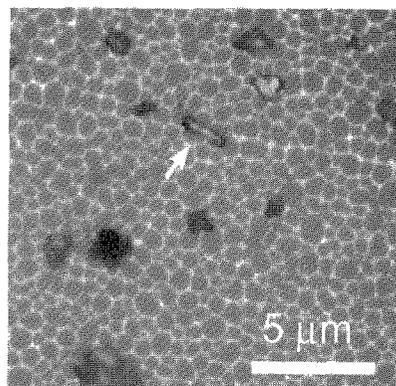


Fig.2 Optical micrograph for the precipitates prepared from a solution with dissolved  $C_{60}C_3H_7N$ -23 mass% $C_{60}C(COOH)_2$  powder.

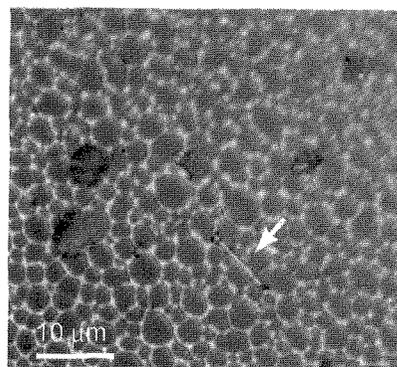


Fig.3 Optical micrograph for the precipitates prepared from a solution with dissolved  $C_{60}C_3H_7N$ -38 mass% $C_{60}C(COOH)_2$  powder.

### 3.2 Nanowhiskers prepared using a solution with dissolved $C_{60}$ -25 mass% $C_{60}[C(COOC_2H_5)_2]$ powder

Fine single crystalline nanowhiskers have been successfully obtained as shown in Fig.4 by using a *m*-xylene solution saturated with fullerene with a composition of  $C_{60}$ -25 mass% $C_{60}[C(COOC_2H_5)_2]$ . The single crystallinity of the nanowhisker can be confirmed by the continuous extinction fringes shown by arrow. The center-to-center distance of the  $C_{60}$  cages that are densely packed along the whisker growth axis was analyzed to be  $D=0.991$  nm by using a FFT pattern (Fig.5) of the HRTEM image for the same whisker of Fig.4.

This  $D$  value is 1.1% smaller than  $D=1.00$  nm of pristine  $C_{60}$  crystals.<sup>9</sup> The  $D$  value was 0.98 nm in a  $C_{60}[C(COOC_2H_5)_2]$  whisker and 1.00 nm in a  $C_{60}$ -5.1 mass%  $C_{60}[C(COOC_2H_5)_2]$  whisker, respectively.<sup>10, 11</sup> These results show that the  $C_{60}$  cages

are densely packed along the whisker growth axis without having the substituent groups between adjoining  $C_{60}$  cages.

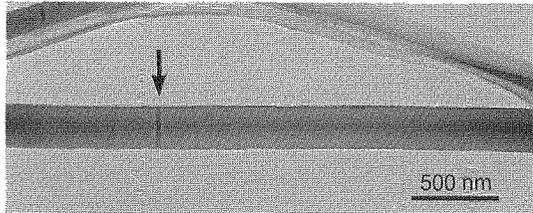


Fig.4 TEM image for a  $C_{60}$  nanowhisker prepared from a *m*-xylene solution saturated with  $C_{60}$ -25 mass% $C_{60}$  [ $C(COOC_2H_5)_2$ ] powder.

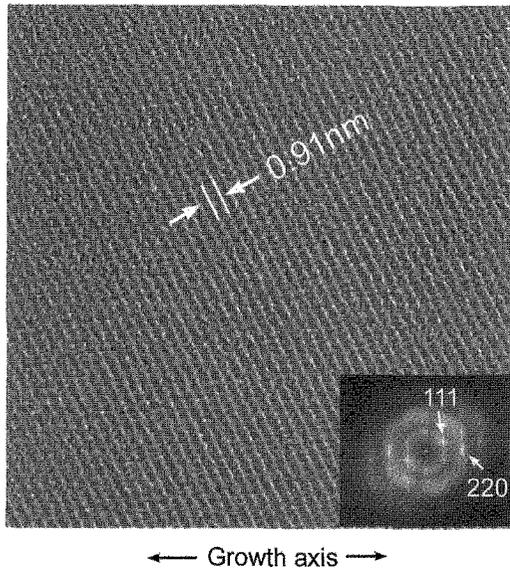


Fig.5 HRTEM image and its FFT pattern for the  $C_{60}$  nanowhisker of Fig.4. The lattice spacing 0.91 nm corresponds to a (111) lattice plane spacing.

### 3.3 Preparation of $C_{70}$ nanotubes and $C_{60}$ - $C_{70}$ two-component nanotubes

As shown in Fig.6, beautiful nanotubes whose wall is composed of  $C_{70}$  molecules have been successfully obtained. A FT-IR analysis proved the formation of  $C_{70}$  nanotubes. It has been found that the  $C_{70}$  nanotubes have an averaged wall thickness of about 120 nm and cannot take the tubular structure when their outer diameter becomes less than about 240 nm owing to the finite wall thickness.

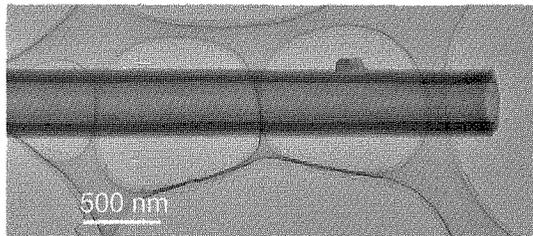


Fig.6 TEM image for a  $C_{70}$  nanotube prepared by the liquid-liquid interfacial precipitation method.

By a X-ray diffraction analysis, the crystal structure of

the  $C_{70}$  nanotubes was found to be a face-centered cubic (fcc) structure with a lattice constant of  $a=1.495$  nm. It has been reported that the  $C_{70}$  crystals exhibit a fcc structure with  $a=1.4974$  nm at 93 °C.<sup>12</sup> These similar lattice constants suggest that  $C_{70}$  molecules of the  $C_{70}$  nanotubes are randomly rotated. Since the  $C_{70}$  crystals change their crystal structure depending on the temperature, the  $C_{70}$  nanotubes are also expected to change their crystal structure and physical properties depending on the temperature.

Fig.7 shows that  $C_{70}$  nanotubes with various diameters can be prepared by the LLIP method.

The  $C_{70}$  tube A has an inner diameter of 344 nm and the  $C_{70}$  tube B has an inner diameter of 656 nm, respectively.  $C_{70}$  tubes with inner diameters greater than 1  $\mu$ m were also observed. The  $C_{70}$  nanotubes may incorporate various size of nanoparticles owing to the wide range of inner diameter. The potential ability of gas storage, especially for hydrogen, is a very interesting property of the  $C_{70}$  nanotubes.

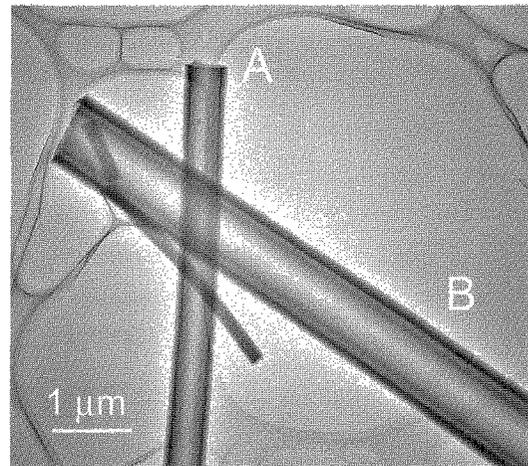


Fig.7 TEM image for  $C_{70}$  (nano)tubes with various outer diameters.

Although, comparing with the above single-component  $C_{70}$  nanotubes, it was more difficult to prepare two-component  $C_{60}$ - $C_{70}$  nanotubes, they have been successfully prepared as shown in Fig.8. The composition of the  $C_{60}$ - $C_{70}$  nanotubes was found to be  $C_{60}$ -15 mol%  $C_{70}$  from their FT-IR analysis.



Fig.8 TEM image for a fullerene nanotube with a composition of  $C_{60}$ -15 mol% $C_{70}$ .

Part of the  $C_{60}$ -15 mol%  $C_{70}$  tube (Fig.8) with an outer diameter of 780 nm is presented in Fig.9 (a). Though Fig.0 (a) shows a tubular structure, the  $C_{60}$ - $C_{70}$  tube has an asymmetric structure about the central tube axis. The magnified image of Fig.9(b) was taken after irradiation with a concentrated electron beam. By the electron beam irradiation, the inner part of the  $C_{60}$ - $C_{70}$  tube was

exfoliated from the surface thin layer with a thickness of 18 nm. The tubular part has an inner diameter of 463 nm and shows irregular domain structures with a size of about 20 nm. The exfoliation of the inner part of the tube is very similar to our previous observation of a capsular structure of  $C_{60}$  that was prepared by use of a  $C_{60}$  toluene solution with added a small amount of  $(\eta^2-C_{60})Pt(PPh_3)_2$ .<sup>6</sup> It is considered that this layer exfoliation was caused by a shrinkage of the inner solvated matrix. The asymmetric morphology about the tube growth axis strongly suggests that the tubular structure was formed by a redissolution of solvated inner whisker core.

The thin surface layer of 18 nm in thickness suggests that the tube wall thickness could be reduced to less than 20 nm in future from the present average thickness of 120 nm by removing the solvated whisker cores.

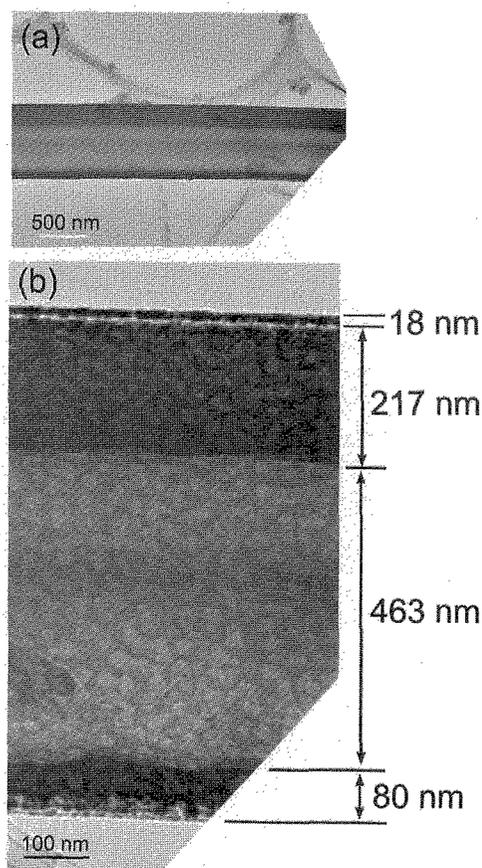


Fig.9 TEM images for a  $C_{70}$  tube. Photo (b) is a magnified image for photo (a) after a concentrated electron beam irradiation.

#### 4. CONCLUSIONS

The present study can be summarized as follows.

- (1) Short needle-like crystals of fullerene derivatives were observed to form, when the mixed *m*-xylene and pyridine solutions with dissolved  $C_{60}C_3H_7N-23 \sim 38$  mass%  $C_{60}C(COOH)_2$  powders were used.
- (2) Two-component fullerene nanowhiskers were successfully prepared by using a *m*-xylene solution

saturated with the  $C_{60} - 25$  mass%  $C_{60} [C(COOC_2H_5)_2]$  powder. This result suggests that direct contacts between the  $C_{60}$  cages along the whisker growth axis were realized in the  $C_{60} - C_{60} [C(COOC_2H_5)_2]$  nanowhiskers.

(3) Two-component nanotubes composed of  $C_{60}$  and  $C_{70}$  molecules ( $C_{60}$ -15mol% $C_{70}$ ) were successfully fabricated by the liquid-liquid interfacial precipitation method.

(4) A core-dissolution mechanism was suggested as the formation mechanism of fullerene nanotubes from the TEM analysis of  $C_{60}$ - $C_{70}$  two-component nanotubes.

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