

Fabrication and Properties of Fullerene Nanowhiskers and Nanofibers

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Abstract : Fine whiskers consisting of C_{60} and C_{70} molecules, i.e., the "fullerene nanowhiskers" can be produced by the liquid-liquid interfacial precipitation method that uses isopropyl alcohol (IPA) and toluene or m-xylene solutions with dissolved fullerenes. The fullerene nanowhiskers grow into long whiskers with aspect ratios > 100 which may be called "fullerene nanofibers" by aging the solutions at around room temperature. The morphology of C_{60} nanowhiskers was drastically changed by adding KOH into IPA. New tubular forms of carbon, 'fullerene shell tubes', were produced by heating the C_{60} nanowhiskers at high temperature in vacuum. A TDS analysis showed that the C_{60} nanowhiskers contain a small amount of impurity solvent toluene.

Key words: C_{60} , C_{70} , fullerene, nanowhisker, nanofiber

1. INTRODUCTION

In the course of preparing a lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$, PZT) sol with a small amount of C_{60} added, fine whiskers of C_{60} , i.e., the " C_{60} nanowhiskers" were discovered.^{1,2} The C_{60} nanowhiskers were defined as the whiskers of C_{60} molecules with diameters of submicrometers. The C_{60} nanowhiskers can be fabricated by forming a liquid-liquid interface of toluene with dissolved C_{60} and isopropyl alcohol. This method is called the 'liquid-liquid interfacial precipitation method (LLIP method)'.³ Not only the C_{60} nanowhiskers but also the nanowhiskers of C_{70} and the C_{60} nanowhiskers doped with iodine could be obtained by the LLIP method.^{4,5}

Although the C_{60} nanowhiskers observed by TEM (transmission electron microscopy) have been single crystalline, the C_{60} whiskers with diameters greater than one micrometer contain polycrystalline whiskers.⁶

The C_{60} whiskers can be flexibly bent with a small curvature radius. For example, a C_{60} nanowhisker with a diameter of 330 nm could be elastically bent with a curvature radius $< 4 \mu m$.⁷ The whiskers of C_{60} showed the lower electrical resistivity with decreasing their diameter.⁶

Although the fullerene nanowhiskers have various unique properties as shown above, their thermal properties have not been substantially investigated. Neither has the influence of impurity elements on the growth and morphology of the fullerene nanowhiskers have not been well understood.

Hence, this paper aims to examine the effect of impurity elements and high-temperature treatment on the structure of the fullerene nanowhiskers.

2. EXPERIMENTAL METHODS

The nanowhiskers/nanofibers of C_{60} and C_{70} were obtained by using the LLIP method that uses the toluene or m-xylene solutions saturated with C_{60} or C_{70} and isopropyl alcohol. C_{60} nanowhiskers were prepared also by using a toluene saturated with C_{60} and an isopropyl alcohol solution of KOH with a concentration of $9.9 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ KOH. The heat treatment of the C_{60} and C_{70} nanowhiskers were conducted in air or in an infrared image furnace evacuated with a rotary pump. The thermal properties of C_{60} nanowhiskers were examined by TG-DTA and TDS (thermal desorption spectrometry).

3. RESULTS AND DISCUSSION

3.1 Morphology of the fullerene nanowhiskers produced by the liquid-liquid interfacial precipitation method

A typical example of single crystalline C_{60} nanowhisker prepared by using m-xylene is given in Fig.1. The C_{60} nanowhisker has a diameter of 94 nm and a length longer than 55 μm . Thinner C_{60} nanowhiskers could be obtained by using m-xylene rather than toluene.

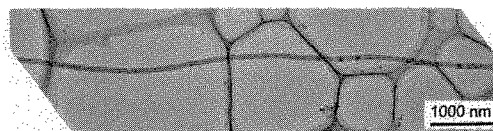


Fig. 1 TEM image of a C_{60} nanowhisker (nanofiber) with 94 nm in diameter prepared by use of a m-xylene solution of C_{60} and isopropyl alcohol.

Fig. 2 shows a HRTEM image for a C_{60} nanowhisker prepared by using m-xylene and its FFT pattern. By

analysing the FFT pattern, it is found that the center-to-center distance D of the C_{60} molecules linked along their close-packed direction, which is parallel to the whisker growth axis, is 0.998 ± 0.008 nm. This D value is slightly smaller than $D=1.002$ nm of pristine fcc C_{60} crystals with $a=1.417$ nm.⁸

Hence, the present example shows that the intercluster distance of C_{60} molecules of the nanowhiskers produced by using *m*-xylene is smaller than that of pristine C_{60} crystals as well as the nanowhiskers produced by using toluene as the solvent.³

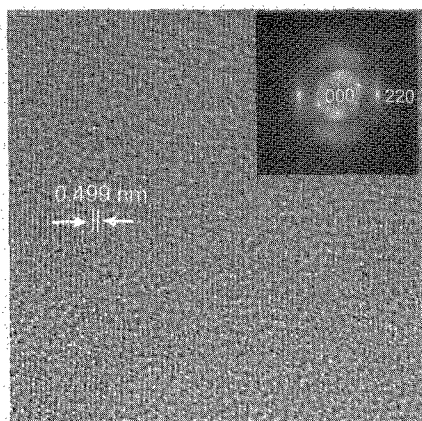


Fig. 2 HRTEM image for a C_{60} nanowhisker produced by using *m*-xylene saturated with C_{60} and isopropyl alcohol.

By aging the solution containing the C_{60} nanowhiskers, they can grow into very long whiskers with an aspect ratio > 100 that may be called ‘ C_{60} nanofibers’. Fig.3(a) shows an example of C_{60} nanofibers fabricated into a sheet by filtering the solution with a paper filter. This is an unwoven sheet composed of randomly oriented C_{60} nanofibers as shown in the magnified image of Fig.3(b).

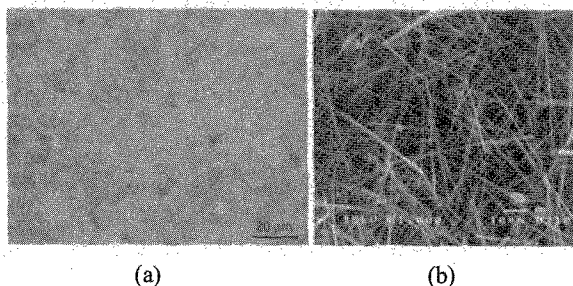


Fig. 3 Optical micrograph (a) and SEM image (b) for a C_{60} sheet with a planar density of ~ 3 mgcm⁻².

The C_{70} nanowhiskers prepared by using *m*-xylene can grow into long nanowhiskers (Fig. 4(a)). The long C_{70} nanowhiskers may be called ‘ C_{70} nanofibers’. Fig.4(b) shows a sheet made of the ‘ C_{70} nanofibers’.

As shown in the thermal desorption spectrometry (TDS) of Fig. 5, toluene is a major impurity element. However, isopropyl alcohol is negligible. The peaks of 1 and 2 indicate the background hydrogen and water, respectively. It is found that nitrogen (peak 3) was released from the C_{60} nanowhiskers at around 200°C. It

is suggested that the nitrogen contained in the C_{60} nanowhiskers was loosely bonded to the C_{60} molecules.

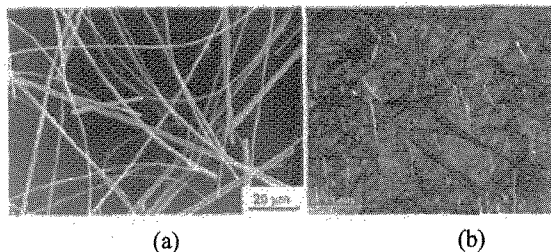


Fig. 4 SEM images of (a) C_{70} nanofibers and (b) C_{70} sheet made of the brown C_{70} nanofibers. Thick needle-like crystals of C_{70} are also observed.

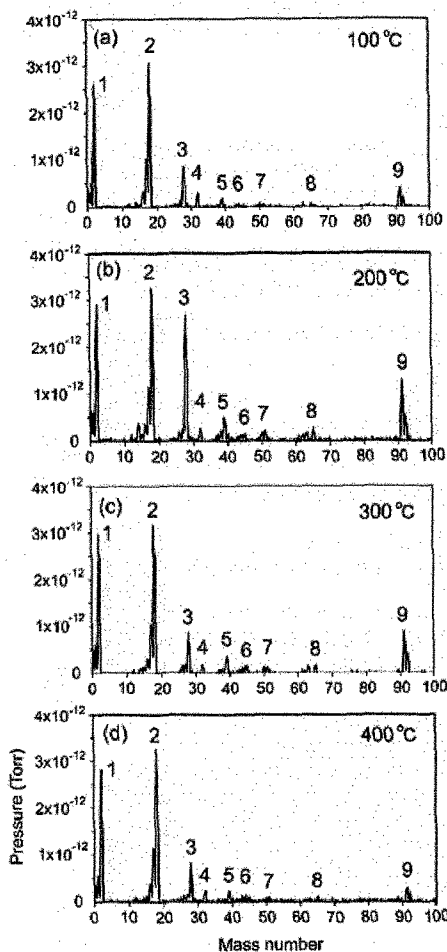


Fig. 5 (a) TDS spectra for the C_{60} nanowhiskers obtained at temperatures between 100°C and 400°C. The peaks 1–4 are identified as 1: H_2 , 2: H_2O , 3: N_2 and 4: O_2 , respectively. The peaks 5, 7, 8 and 9 correspond to toluene. Peak 6 corresponds to isopropyl alcohol.

3.2 Structure of the heat-treated C_{60} and C_{70} nanowhiskers

A result of TG-DTA analysis in air is shown in Fig. 6 for the C_{60} nanowhiskers prepared by use of toluene saturated with C_{60} . It is found that the C_{60} nanowhiskers begin to decompose from about 420°C. The DTA curve shows a second exothermic peak at around 590°C. This

result suggests that the LLIP method can produce the C₆₀ nanowhiskers with high heat resistance. Actually as shown in Fig. 7, a part of the C₆₀ nanowhiskers heated at 900°C retained their crystalline structure, although most of them became amorphous.

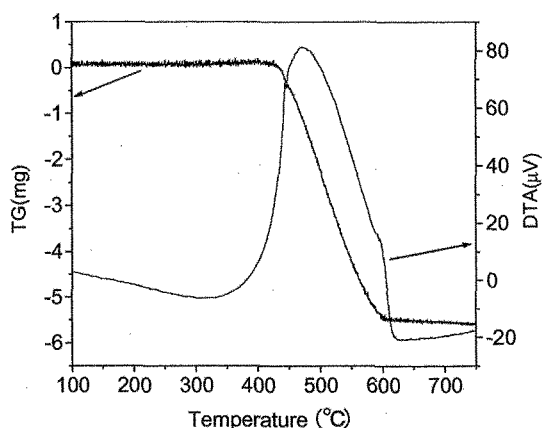


Fig. 6 TG-DTA curves for the C₆₀ nanowhiskers measured in air.

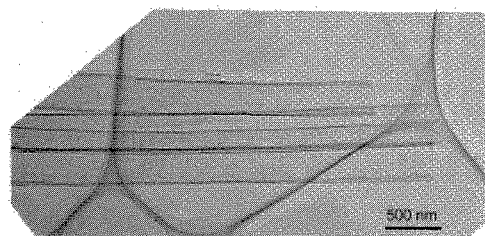


Fig. 7 TEM image of the 'fullerene shell tubes' prepared by heating the C₆₀ nanowhiskers at 600°C for 30 min in vacuum.

On the other hand, a part of the C₆₀ nanowhiskers heated at 600°C for 30 min in vacuum formed the tubular structures which may be called 'C₆₀ shell tubes' as shown in Fig. 8. The C₆₀ shell tubes show their original crystal habit planes. The C₆₀ shells have been known to form by heating C₆₀ crystals in vacuum.⁹

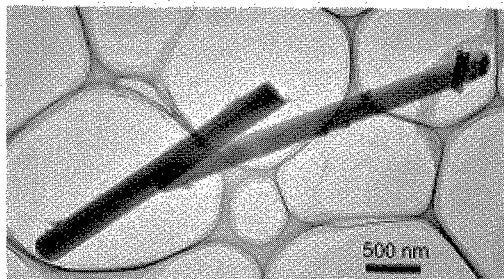


Fig. 8 TEM image of the C₆₀ nanowhiskers heated at 900°C for 30 min in vacuum.

The C₇₀ nanowhiskers produced by using m-xylene were heat-treated in air at 300°C. Fig. 9 shows that the C₇₀ nanowhisker is highly porous. Such porous C₇₀

nanowhiskers may be useful as some catalyst carriers.

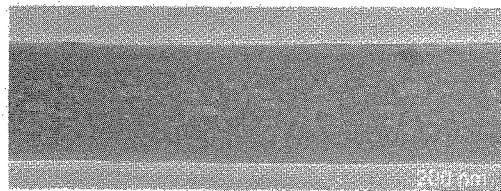


Fig. 9 TEM image of a C₇₀ nanowhisker heat-treated at 300°C in air.

Table 1 summarizes the crystallographic data of the heat-treated C₇₀ nanowhiskers that were indexed based on fcc systems. The heat-treated C₇₀ nanowhiskers have the d-spacings greater than those of the as-prepared C₇₀ nanowhiskers. The center-to-center distance D between adjoining C₇₀ cages is 0.526 nm in the heat-treated C₇₀ nanowhisker. This D value is very close to D=0.529 nm of a fcc C₇₀ crystal.¹⁰ This result shows that the C₇₀ molecules of the heat-treated C₇₀ nanowhisker have developed spherically random orientation by the heat treatment.

Table 1 Lattice-plane spacings (d,nm) of (a) the C₇₀ nanowhisker heat-treated at 300°C in air and (b) the as-prepared C₇₀ nanowhiskers.⁴

(h k l)	(a)	(b)
(111)	0.890±0.003	0.844±0.080
(002)	0.829±0.045	0.710±0.043
(220)	0.526±0.003	0.513±0.031

3.3 Structure of the C₆₀ nanowhiskers produced by using isopropyl alcohol with dissolved KOH

TEM observations were performed for the samples prepared by use of a concentrated toluene solution of C₆₀ and IPA with dissolved KOH.

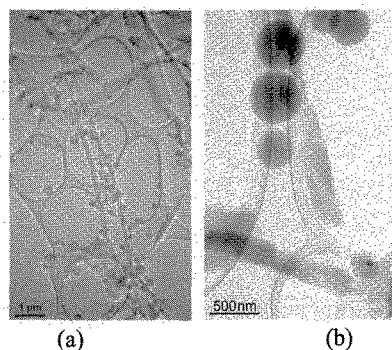


Fig. 10 TEM images of C₆₀ precipitates prepared by using IPA with a concentration of $3.3 \times 10^{-3} \text{ molL}^{-1}$ KOH (a) and (b) IPA with a concentration of $9.9 \times 10^{-3} \text{ molL}^{-1}$ KOH, respectively.

Fig. 10(a) shows the formation of C₆₀ nanowhiskers of ~200 nm in diameter by the use of IPA with the smaller concentration of KOH. However, the linear-shaped C₆₀ nanowhisker was negligible when the KOH concentration was increased as shown in Fig. 10(b). This example clearly shows that the concentration

of KOH strongly influences the morphology of the precipitated C₆₀.

Fig.11 shows a HRTEM analysis of a C₆₀ nanowhisker prepared by use of IPA with a concentration of 3.3×10^{-3} molL⁻¹ KOH. The FFT pattern was indexed with a cubic system.

Table 2 shows the d-spacings calculated from the FFT pattern of Fig.11(b) and five selected area electron diffraction patterns (SAEDPs) of different C₆₀ nanowhiskers sampled from the same glass bottle. The d-spacings of (111) and (220) planes are found to have markedly shrunk from those of pristine fcc C₆₀ crystals. The d-spacing along the growth axis is about 2–6 % shrunk from the value of pristine C₆₀.

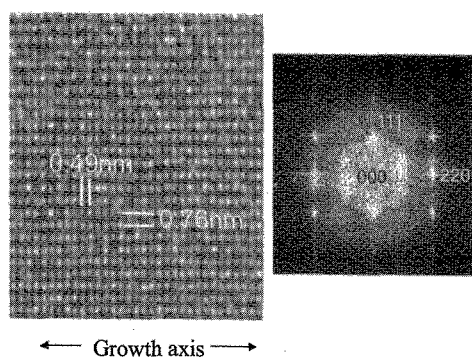


Fig. 11 (a)HRTEM image of a C₆₀ nanowhisker prepared by use of IPA with a concentration of 3.3×10^{-3} molL⁻¹ KOH and (b) its FFT pattern.

Table 2 Lattice-plane spacings (d,nm) calculated from the FFT pattern of Fig.11 (b) and the SAEDPs of the K-doped C₆₀ nanowhiskers and the corresponding d-spacings of pristine C₆₀ crystals.

(hkl)	Fig. 11(b)	SAEDPs	pristine C ₆₀ crystals ^a
111	0.76	0.777±0.022	0.816
002	---	0.762±0.033	0.709
220	0.49	0.470±0.005	0.501

The large shrinkage in the close-packed direction of the whiskers suggests a formation of chemical bonding between adjoining C₆₀ molecules

The mechanism of shrinkage in the intercluster distance between the C₆₀ molecules of the whiskers has not been clarified. Tachibana et al. showed that the C₆₀ molecules in the as-prepared C₆₀ nanowhiskers are bonded via weak van der Waals force.¹¹ Hence, it is supposed that the large shrinkage in the d₂₂₀ spacing was promoted by the irradiation of light or electron beam during observation by TEM.¹²

5. CONCLUSIONS

The present study can be summarized as follows.

- (1) Fullerene nanowhiskers have been successfully prepared by using the m-xylene solutions of C₆₀ and C₇₀ as well as the toluene solutions of C₆₀ and C₇₀.
- (2) Tubular structures of carbon, 'fullerene shell tubes'

have been prepared by heating the C₆₀ nanowhiskers in vacuum.

(3) A large shrinkage in the intercluster distance of C₆₀ molecules along the whisker growth axis was observed in the C₆₀ nanowhiskers prepared by using isopropyl alcohol with dissolved KOH.

(4) The C₇₀ nanowhiskers fired at 300°C showed a highly porous structure. The intercluster distance of C₇₀ molecules along the whisker growth axis in these nanowhiskers was very close to that of a fcc C₇₀ crystal.

ACKNOWLEDGEMENT

The authors are grateful to Mr.H.Tsunakawa and Dr.C.Iwamoto for the use of HRTEM (The University of Tokyo).

This research was financially supported by a Grant in Aid for Scientific Research of the Ministry of Education, Culture, Sports, Science and Technology of Japan (Projects 14350367 and 15651063).

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(Received October 10, 2003; Accepted October 31, 2003)