Morphology of C_{60} nanotubes fabricated by the liquid–liquid interfacial precipitation method

Jun-ichi Minato^{a,*}, Kun’ichi Miyazawa^{a}, Tadatomo Suga^{b}

^{a}Ecomaterials Center, National Institute for Materials Science, Namiki 1-1, Tsukuba 305-0044, Japan
^{b}Department of Precision Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received 12 January 2005; revised 10 February 2005; accepted 10 February 2005
Available online 14 July 2005

Abstract

Single crystalline C_{60} fullerene nanowhiskers are formed by adding isopropyl alcohol gently to fullerene saturated solutions. The method is called the liquid–liquid interfacial precipitation method. In the present study, observation using transmission electron microscope was made for C_{60} nanowhiskers with hollow structure, i.e. C_{60} fullerene nanotubes fabricated by the modification of liquid–liquid interfacial precipitation method using pyridine as solvent. After adding isopropyl alcohol to the C_{60} solution in the glass bottles, ultrasonic dispersion was applied for 1 min and then the bottles were kept at 10°C. Within 24 h, fibrous solids with the length larger than several millimeters and the diameters ranging from submicrons to 1 mm were precipitated. For the transmission electron microscope study, the samples were pulverized by the ultrasonic dispersion. Under the transmission electron microscope, tubular morphology was usually observed for the whiskers with the diameters larger than 200 nm and hardly observed for those with the diameters smaller than 200 nm; both the C_{60} fullerene nanotubes and the fullerene C_{60} nanowhiskers were in crystalline state. Since partly tubular structures were sometimes observed at the end of the C_{60} fullerene nanowhiskers, the mechanism for the formation of tubular morphology is suggested to be a dissolution process after the crystal growth. When the samples were kept in the glass bottles for several hours after the pulverization, closing of nanotubes at the ends was observed for relatively smaller nanotubes in diameter. For relatively larger nanotubes in diameter, zigzag thinning of tube wall edges was observed. It is thus expected that subsequent growth or dissolution occurred at the end of the pulverized C_{60} nanotubes, which may be an effective way to control the shape of tubes. The C_{60} nanotubes presented here will be useful as adsorbents, catalysts, and membranes.

Keywords: Fullerene; C_{60}; Nanowhisker; Nanotube; Liquid–liquid interfacial precipitation method; Transmission electron microscopy

1. Introduction

Since the discovery of the method to manufacture bulk fullerenes in macroscopic quantities, many crystallographic studies have been made [1]. Fullerenes are soluble in many solvents such as benzene, hexane, and CS_{2}, and crystallize to form solid solvates with these solvents. Some of these solvated structures are not air stable and rapidly lose solvent by evaporation [2]. Some other solvated crystals, on the other hand, are shown to be stable in air for 9 years at room temperature in the dark [3]. Depending on their structure, variety of morphologies is obtained for these solid solvates; they are sometimes large and well-defined polyhedral ones and are quite different from those expected for the pure solid C_{60} of the face-centered cubic structure [1,2].

Fullerene nanowhiskers are fibrous fullerene single crystals with diameters as small as submicrons [4]. The fabrication method of the fullerene nanowhiskers is quite simple and unique. They are precipitated at the liquid–liquid interface of fullerene-dissolved solution and isopropyl alcohol (liquid–liquid interfacial precipitation method [5]). By the liquid–liquid interfacial precipitation method, various fullerene nanowhiskers have been successfully fabricated such as C_{70} nanowhiskers [6], iodine-doped C_{60} nanowhiskers [7], and nanowhiskers of fullerene derivatives [8,9]. The structure of fullerene nanowhiskers is based on the face-centered cubic packing of fullerene molecules as well as the pristine C_{60} crystals. The growth axis of the fullerene nanowhiskers is parallel to [\bar{1}10],
i.e. a close-packed direction of face-centered cubic packing of fullerene molecules, with the slightly shorter intermolecular distance by a few %. This has been explained in relation with the van der Waals polymerization of fullerene molecules along the direction [10].

Recently, fullerene nanowhiskers with hollow structures, which may be called as fullerene nanotubes, have been found [10,11]. They have wall structures made of fullerene molecules. With the modification to the liquid–liquid interfacial precipitation method, the hollow fullerene nanowhiskers have been successfully fabricated either by mixing \((\eta^2-C_{60})\text{Pt}(\text{PPh}_3)_2\) with the \(C_{60}\) [12], or by using pyridine solution of \(C_{70}\) fullerenes [11]. However, the latter method was not directly applicable to the formation of pure \(C_{60}\) fullerene nanotubes because the precipitation of fibrous material hardly took place. The another way to obtain tubular structure was the careful sublimation of fullerene molecules by heating after the crystal growth of \(C_{60}\) fullerene nanowhiskers; however, heating process sometimes destroyed fullerene molecules leaving the shell of amorphous carbon [13]. When the application of the fullerene nanotubes is taken into account, it is desired to predict the property change of fullerene nanotubes with their composition of fullerene species. For this purpose, an establishment of the way to fabricate pure \(C_{60}\) fullerene nanotubes is needed.

In this paper, we propose a reproducible fabrication method of purer \(C_{60}\) fullerene nanotubes by the modification of liquid–liquid interfacial precipitation method. Since the diffusion state at the liquid–liquid interface seemed to affect the growth and the quality of products, controlled mixing was applied ultrasonically. Attempts to control the morphology of \(C_{60}\) fullerene nanotubes were also reported. Characterization by X-ray diffraction (XRD) and transmission electron microscopy showed that fullerene nanotubes were grown as solvated structure with hexagonal symmetry followed by the phase transformation into face-centered cubic structure due to the evaporation of solvent molecules. Unlike the other carbon substances, fullerene nanotubes are re-dissolved in proper solvents, and maybe useful not only as adsorbents and catalysts but also as templates for the various forms of materials such as fibers and membranes.

2. Experimental

As received, pristine \(C_{60}\) powder (MTR Ltd. 99.5%) was dissolved in pyridine. Twenty seven milliliters of isopropl alcohol was added to each 3 mL of pyridine solution of \(C_{60}\) in the glass bottles; all solutions and bottles were kept at about 10 °C during the experiments. To obtain suitable diffusion at the interface, insertion of ultrasonic dispersion for 1 min was made after the addition of isopropl alcohol.

Morphological observations were performed using an ordinary optical microscope and a transmission electron microscope (TEM; JEOL, JEM-2000EX). The specimens in the glass bottles were mounted either on the slide glass or onto the microgrids after the ultrasonic pulverization for 1 min. XRD spectra were obtained using an X-ray diffractometer (RIGAKU, RINT2000) with Cu Kα radiation. For the measurement, the specimens were directly mounted on a glass sample holder immediately after the sampling from the glass bottles to monitor the structural changes during the drying process.

3. Results

Although the precipitation of the fibrous material occurs within a day, completion of the growth seems to require several weeks. When the \(C_{60}\) nanowhiskers were sufficiently grown, the bundles of them were easily recognized by eye (Fig. 1(a)). Optical microscopy revealed the bundles consisted of fibers of about 1 μm in diameter and several millimeters in length (Fig. 1(b)). Dissolution in toluene, \(m\)-xylene, or pyridine that are known as good solvents of fullerenes well demonstrated that the specimens are really

![Fig. 1. (a) Photograph of \(C_{60}\) nanotubes grown by forming liquid–liquid interface between pyridine saturated with \(C_{60}\) and isopropyl alcohol and (b) optical photomicrograph of \(C_{60}\) nanotubes.](image_url)
composed of $C_{60}$ fullerene molecules by giving characteristic colors of $C_{60}$ fullerenes in these solvents. On the other hand, the specimens could not be dissolved in acetone, isopropyl alcohol, or water.

Fig. 2 shows TEM images of the $C_{60}$ fullerene nanotubes that were drawn from the glass bottle 1 min after the pulverization. By the pulverization, open edges are observed to confirm the tubular structure of the specimen. In the figure, the diameter of $C_{60}$ fullerene nanotubes varies in the range between several hundreds of nanometers and a few micrometers. On the other hand, those with diameters smaller than 200 nm seldom showed tubular structure. This means that a moderately large diameter is needed for the formation of $C_{60}$ fullerene nanotubes at the present formation conditions.

Re-growth of the $C_{60}$ fullerene nanotubes were observed when the glass bottle was kept at $10^8$ °C after the ultrasonic pulverization. For example, $C_{60}$ nanotubes with diameters smaller than 1 μm usually showed sharpened and closed ends 20 min after the pulverization (Fig. 3). Those with diameters larger than 1 micrometer, on the other hand, showed open ends (Fig. 4). They also showed relatively thick tube walls near the ends and zigzag thinning at the wall edges. These morphological changes indicate that subsequent growth took place at the fractured surface by the ultrasonic pulverization. Further growth for 12 h resulted in the thinner nanowhiskers connected to the closed edges of $C_{60}$ nanotubes (Fig. 5). The smaller diameter of the nanowhisker part than that of nanotube part means the interruption of the crystal growth. Probably, the growth conditions have changed as the number of the edges for the crystal growth significantly increased by the pulverization.

Electron diffraction pattern shows that the $C_{60}$ nanotubes are in crystalline state (Fig. 6(a)). The pattern was indexed as face-centered cubic structure of $C_{60}$ and the direction of growth axis was parallel to $\langle 1\bar{1}0 \rangle$, which is consistent with previous observations for fullerene nanowhiskers grown using toluene as solvent [5,6] and $C_{70}$ fullerene nanotubes [11]. For $C_{60}$ fullerene nanotubes, however, diffraction spot universally indicated streaks and sometimes have maxima in the direction perpendicular to the growth axis that are indicated by arrows in Fig. 6(a). Streaks and maxima in the electron diffraction pattern are usually caused by the stacking faults, crystal morphology effect, elastic strain effect, or twinning [14]. For fullerene crystals, a possible cause for the streaks is the phase change resulting in twins as they are known to crystallize
in the solvated structure and to change into face-centered cubic structure by the evaporation of solvent molecules [3]. In the present case, they are explained by assuming that another diffraction pattern (along $\frac{1}{2}$[110]) is overlapped to the ordinary one along [110] with a common direction $\frac{1}{2}$[110] as shown in Fig. 6(b).

To confirm the solvated structure and the phase transformation, the change in X-ray diffraction pattern with time was examined. The XRD pattern taken 15 min after the sampling from the glass bottles showed sharp peaks that were different from those of pristine $C_{60}$ (Fig. 7(a)). These peaks were indexed by assuming hexagonal symmetry with cell dimension $a = 1.539$ nm. These peaks rapidly disappeared and broad peaks appeared at the same position as pristine $C_{60}$ (Fig. 7(b) and (c)). The phenomenon indicates that $C_{60}$ nanotubes are grown as hexagonal, solvated structure along the $c$-axes and then the structure was changed to face-centered cubic packing of $C_{60}$ molecules by the evaporation of solvent molecules in air.

4. Discussion

Present observation showed a possibility to fabricate and control various morphologies of $C_{60}$ fullerene nanotubes by the combination of ultrasonic pulverization with the subsequent crystal growth. The method may be used for the encapsulation of molecules and clusters in the fullerene nanotubes, and for the reaction within them. Unlike the other carbon substances, fullerene nanotubes have an advantage to be re-dissolved in proper solvents. This enables fullerene nanotubes to be used as templates for the various forms of materials such as fibers and membranes.

In TEM study, a selected area electron diffraction image was observed consisting of two patterns corresponding to those with incident beam parallel to [$1\bar{1}2$] and [110] as shown in Fig. 6. Since the angle between the direction [110] and [$1\bar{1}2$] is $125.26^\circ$ which is close to $2\pi/3$, we can assume three crystallographic orientations related with each other by about $2\pi/3$ around the growth axis [$1\bar{1}0$]. In addition, the solvated structure and the phase transformation were observed in XRD study. Since the solvated structure was indexed as hexagonal symmetry, twinning by the phase transformation from hexagonal to face-centered cubic structure is assumed for each $C_{60}$ fullerene nanotube.

Although the solvated structure has not been fully determined, a possible one may be represented by the simple hexagonal packing of $C_{60}$ molecules as shown in Fig. 8.

The structure is less dense than that of face-centered cubic
packing of C_{60}, and can contain large amount of solvent molecules, which may be related to the formation of the tubular structure. When the transformation takes place in the way that C_{60} sheets parallel to one set of prism faces are shift along the direction of the whisker’s growth axis, a face-centered cubic packing results. Since there are three sets of prism faces in a hexagonal packing, three orientations are possible for the face-centered cubic structure finally resulting in the twinned structure as observed in the electron diffraction pattern.

The formation of the tubular structure of the fullerene nanotubes is not completely described. A previous study proposed a possible mechanism for the C_{70} nanotubes that they are first grown as nanowhiskers and then changed into hollow structure through the dissolution of the inner part [11]. In the present study, the partly hollow structures at the ends were observed as shown in Fig. 9 by reducing the proportion of isopropyl alcohol added to the pyridine solution of C_{60}. This may indicate that the dissolution is also one of the important factors for the formation of C_{60} nanotubes.

The crystal growth at the tube edges after the pulverization suggests that the tubular structure, or at least the core–shell structure [10,11], was already formed before the sampling from the glass bottles. However, the phase transformation during the evaporation of solvent molecules indicates that the rearrangement of C_{60} molecules took place
after the sampling. Probably, the actual mechanism of the tubular structure is related to both the phase transformation and the dissolution. A further comprehension of these may enable us to control the morphologies of C₆₀ nanotubes for the various applications.

5. Conclusion

Hollow fullerene nanotubes were fabricated using pure C₆₀. The C₆₀ fullerene nanotubes were precipitated and grown by the mixing of pyridine solution of C₆₀ and isopropyl alcohol. By the combination of ultrasonic pulverization with the subsequent crystal growth, various morphologies of C₆₀ fullerene nanotubes were obtained. The C₆₀ nanotubes grew as solvated structure with hexagonal symmetry followed by the phase transformation into face-centered cubic structure due to the evaporation of solvent molecules. Although the tubular structure of the fullerene nanotubes has not been explained completely, both the phase transformation and the dissolution at the edge may be related to the formation process.

Since the fullerene nanotubes can be re-dissolved in proper solvents, they may be useful not only as adsorbents and catalysts but also as templates for the various forms of materials such as fibers and membranes.

Acknowledgements

The authors are grateful to Mr. K. Kurashima (NIMS) for expert advice on transmission electron microscope study. Part of this research was financially supported by the Grant in Aid for Scientific Research of the Ministry of Education, Culture, Sports, Science, and Technology of Japan (Project Nos. 14350367 and 15651063).

References

[1] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, Solid C₆₀: a new form of carbon, Nature 347 (1990) 354–358.
[2] H. He, J. Barras, J. Foulkes, J. Klinowski, Solid-state NMR studies of fullerene C₆₀/benzene solvates, J. Phys. Chem. B 101 (2) (1997) 117–122.
[3] S. Toscani, H. Allouchi, J.L.L. Tamarit, D.O. López, M. Barrio, V. Agafonov, A. Rassat, H. Szwarc, R. Céolin, Decagonal C₆₀ crystals grown from n-hexane solutions: solid-state and aging studies, Chem. Phys. Lett. 330 (2000) 491–496.
[4] K. Miyazawa, A. Obayashi, M. Kuwabara, C₆₀ nanowhiskers in a mixture of lead zirconate titanate sol-C₆₀ toluene solution, J. Am. Ceram. Soc. 84 (12) (2001) 3037–3039.
[5] K. Miyazawa, Y. Kuwasaki, A. Obayashi, M. Kuwabara, C₆₀ nanowhiskers formed by the liquid–liquid interfacial precipitation method, J. Mater. Res. 17 (1) (2002) 83–88.
[6] K. Miyazawa, C₇₀ nanowhiskers fabricated by forming liquid/liquid interfaces in the systems of toluene solution of C₇₀ and isopropyl alcohol, J. Am. Ceram. Soc. 85 (5) (2002) 1297–1299.
[7] K. Miyazawa, K. Hamamoto, Fabrication of iodine-doped C₆₀ whiskers by the use of liquid–liquid interfacial precipitation method, J. Mater. Res. 17 (9) (2002) 2205–2208.
[8] K. Miyazawa, T. Mashino, T. Suga, Structural characterization of the C₆₀[C(COOC₂H₅)₂] whiskers prepared by the liquid–liquid interfacial precipitation method, J. Mater. Res. 18 (11) (2003) 2730–2735.
[9] K. Miyazawa, T. Mashino, T. Suga, Liquid phase synthesis of the nanowhiskers of fullerene derivatives, Trans. Mater. Res. Soc. Jpn 29 (5) (2004) 537–540.
[10] K. Miyazawa, M. Fujino, J. Minato, T. Yoshii, T. Kizuka, T. Suga, Structure and properties of fullerene nanowhiskers prepared by the liquid–liquid interfacial precipitation method, Proc. SPIE 5648 (2005) 224–234.
[11] K. Miyazawa, J. Minato, T. Yoshii, M. Fujino, T. Suga, Structural characterization of the fullerene nanotubes prepared by the liquid–liquid interfacial precipitation method, J. Mater. Res. 20 (3) (2005) 688–695.
[12] K. Miyazawa, T. Suga, Transmission electron microscopy investigation of fullerene nanowhiskers and needle-like precipitates formed by using C₆₀ and (η⁵-C₆₀)Pt(PPh₃)₂, J. Mater. Res. 19 (8) (2004) 2410–2414.
[13] K. Miyazawa, C. Nishimura, M. Fujino, T. Suga, T. Yoshii, Fabrication and properties of fullerene nanowhiskers and nanofibers, Trans. Mater. Res. Soc. Jpn 29 (5) (2004) 1965–1968.
[14] P.B. Hirsch, A. Howie, R.B. Nicholson, D.W. Pashley, M.J. Whelan, Electron Microscopy of Thin Crystals, Butterworth, London, 1967.