Characterization of fullerene nanotubes prepared by the liquid–liquid interfacial precipitation method

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Abstract

C\textsubscript{70} nanotubes were prepared by using pyridine and isopropyl alcohol and heated in air at 250\thinspace ^\circ\thinspace C in order to eliminate the contained solvents ‘heat treated C\textsubscript{70}’. The C\textsubscript{70} nanotubes were also successfully prepared by use of pyridine and isobutyl alcohol. The C\textsubscript{70} nanotubes heated at 1100\thinspace ^\circ\thinspace C in vacuum became amorphous carbon, but retained the tubular structure. The structural characteristics of these C\textsubscript{70} nanotubes are observed through their high-resolution transmission electron microscopy.

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1. Introduction

Carbon nanotubes (CNTs) discovered by Iijima in 1991 \cite{1} have been extensively investigated for their wide application in energy, electronics, mechanics, composites, catalysts, pharmaceuticals and so on. The CNTs are usually composed of cylindrical graphene sheets. However, preparations of carbon nanotubes with amorphous carbon walls have been reported. The amorphous carbon nanotubes are expected to be used as promising hydrogen storage materials \cite{2}.

On the other hand, ‘fullerene nanowhiskers’ are the fine crystalline fibers that are composed of fullerene molecules and have diameters in the order of nanometers \cite{3}. Until now, we have reported various kinds of fullerene nanowhiskers composed C\textsubscript{60}, C\textsubscript{70} and C\textsubscript{60} [C(COOC\textsubscript{2}H\textsubscript{5})\textsubscript{2}] molecules \cite{3–5}. The fullerene nanowhiskers can be prepared by the liquid–liquid interfacial precipitation method (LLIP method) \cite{3}. In the LLIP method, the fullerene nanowhiskers nucleate at the interface between a fullerene-saturated toluene (or m-xylene) solution and isopropyl alcohol in a glass bottle at room temperature, and the fullerene nanowhiskers grow in the glass bottle, consuming the fullerene molecules in the solution. Recently, Tachibana et al. showed that the growth of C\textsubscript{60} nanowhiskers can be enhanced under illumination of visible light \cite{6}. It was also shown that single crystalline C\textsubscript{60} nanowhiskers with dissolved C\textsubscript{60}[C(COOC\textsubscript{2}H\textsubscript{5})\textsubscript{2}] could be fabricated by the LLIP method \cite{7}.

Not only the solid fullerene nanowhiskers but also capsular needle-like crystals of C\textsubscript{60} could be prepared by the LLIP method using a C\textsubscript{60} powder containing a small amount of platinum derivative of C\textsubscript{60}, (\textgreek{n}\textsuperscript{2}–C\textsubscript{60})Pt(PPh\textsubscript{3})\textsubscript{2} \cite{8}. The capsular C\textsubscript{60} crystals were shown to have single crystalline walls of C\textsubscript{60}. Furthermore, we have successfully fabricated ‘C\textsubscript{60} nanotubes’ whose walls are composed of C\textsubscript{60} molecules through the LLIP method by using a C\textsubscript{60}-saturated toluene solution with added (\textgreek{n}\textsuperscript{2}–C\textsubscript{60})Pt(PPh\textsubscript{3})\textsubscript{2} \cite{9}.

We also showed that the C\textsubscript{60} nanowhiskers could be converted to hollow nano carbon tubes by heating in vacuum \cite{8}. The hollow carbon tubes were named ‘fullerene shell tubes’, following the naming of ‘C\textsubscript{60} shell’ \cite{10}.

In addition, we also showed that various forms of needle-like crystals of fullerene molecules could be produced by the LLIP method. Further, recently we have successfully prepared the nanotubes composed of C\textsubscript{70} molecules and the structural characteristics of as-prepared C\textsubscript{70} nanotubes were presented \cite{11}. The as-prepared C\textsubscript{70} nanotubes had red
brownish and metallic colour as shown in Fig. 1. By an X-ray diffraction experiment, the as-prepared C70 nanotubes were found to have a face-centered cubic (fcc) structure with a lattice constant of \( a = 1.495 \pm 0.015 \text{ nm} \) which is very close to the lattice constant \( a = 1.4974 \text{ nm} \) of C70 crystals measured at 93 °C [12]. This fact indicates that C70 molecules are randomly rotated in the C70 nanotube walls.

Although the above C70 nanotubes were prepared by use of isopropyl alcohol (IPA) for the nucleation agent of C70 crystals and pyridine for the solvent of C70, various kinds of alcohols in addition to isopropyl alcohol are expected to be applicable to preparing the C70 nanotubes. The present paper also shows that the C70 nanotubes can be fabricated by use of isobutyl alcohol (IBA) as well, and their structural characteristics are discussed in comparison with the C70 nanotubes prepared by the use of IPA through their transmission electron microscopy (TEM) observations.

Since, the as-prepared C70 nanotubes contain impurity solvent molecules, it is necessary to eliminate the contained solvent molecules in order to stabilize the physical properties of the C70 nanotubes in air. Although the elimination of solvent could be done by heating in vacuum or in air, the heat treatment in air was more convenient and practical. Hence, as an initial trial for the solvent elimination, the C70 nanotubes prepared by use of IPA and pyridine were heated at 250 °C for 4 h in an electric furnace in air.

The C70 nanotubes were examined by high-resolution transmission electron microscopy (HRTEM, JEM-4010, 400 kV, JEOL, Japan) and FT-IR (Valor III, JASCO, Japan). In the TEM observation, the C70 nanotubes were ultrasonically dispersed in methanol and pipetted on to carbon microgrids.

The FT-IR spectra for the nanotubes and powder of C70 (99.5%, MTR Co.) were obtained by preparing their pellets mixed with KBr.

The heat treatment of C70 nanotubes was done at 1100 °C for 1 h in an evacuated fused silica tube by use of a muffle furnace with a heating rate of 20 °C min⁻¹.

2. Experimental procedure

The C70 nanotubes were fabricated by using pyridine for the solvent of C70. 2 ml of pyridine solution saturated with C70 (99.5%, MTR Co., Ohio, USA) was put into a 9 ml glass bottle and 6 ml of isopropyl alcohol was gently added to the C70 pyridine solution at 10 °C to form a liquid–liquid interface. The glass bottle was allowed to stand for two weeks at 10 °C in an incubator with a transparent plastic window (SANYO MIR-153, SANYO Electric Co., Ltd, Tokyo, Japan). The preparation of C70 nanotubes by use of isobutyl alcohol and a C70-saturated pyridine solution was similarly done through the LLIP method.

In the drying experiment, the C70 nanotubes prepared by use of IPA and pyridine were heated at 250 °C for 4 h in an electric furnace in air.

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3. Results and discussion

3.1. C70 nanotubes prepared by use of isobutyl alcohol

C70 nanotubes have been successfully prepared by use of IBA and the pyridine solution saturated with C70 as shown in the TEM image of Fig. 2(a). The average wall thickness of the C70 nanotube of Fig. 2 is 112 ± 36 nm which is very close to the wall thickness of 113 ± 18 nm of the C70
nanotubes prepared by use of IPA [11]. Although this result suggests that the wall thickness of C70 nanotubes has similar values and does not depend on the kind of alcohol, more data is necessary to confirm the result, testing various alcohols other than IPA and IBA.

As shown in the selected area electron diffraction pattern (SAEDP) of Fig. 2(b), it is suggested that the C70 nanotube has a single crystalline wall. The single crystallinity of C70 nanotube wall is also suggested by the continuous extinction fringes observed in the marked place of the C70 nanotube of Fig. 4(a). However, the 111 spots (Fig. 2(b)) elongated along the [0 0 1] direction indicates that the C70 nanotube wall is composed of thin layers and contain a high density of planar faults. This laminar structure of the wall can be observed in the cross-sectional edge image of Fig. 3. The laminar wall structure is also observed in another example of the C70 nanotube of Fig. 4(b). It is also shown that solid C70 nanowhiskers have the laminar structure [14]. The laminar structure common to both the C70 nanotubes and C70 nanowhiskers suggests that the C70 nanowhiskers and C70 nanotubes have a resembled formation mechanism. The hollow structure of the C70 nanotubes may have been caused by a dissolution of solvated inside cores of C70 nanowhiskers.

As shown in the HRTEM image of Fig. 5(a) for the C70 nanotube of Fig. 2, the C70 nanotube wall with a thickness of about 80 nm has a disordered surface layer with a thickness of about 20 nm. Fig. 5(b) shows a Fast Fourier Transform (FFT) pattern for the enclosed part of the wall, where the FFT spots are indexed by assuming an orthorhombic structure. Five FFT patterns including Fig. 5(b) are analyzed for the tube wall and the lattice plane spacings derived from the FFT patterns are summarized in Table 1.

### 3.2. Heat-treated C70 nanotubes

FT-IR spectra for the heat-treated C70 nanotubes, the as-prepared C70 nanotubes (Fig. 1) and the pure C70 powder (99.5%), are shown in Fig. 6. The FT-IR spectrum (b) for the as-prepared C70 nanotubes show the absorption peaks characteristic to C70 molecules at 458, 535, 579, 642, 674, 796, 1086, 1135 and 1431 cm\(^{-1}\). The heat-treated C70 nanotubes show the corresponding absorption peaks at 578, 641, 674, 796, 1060 and 1430 cm\(^{-1}\), which confirms the remaining C70 molecules in the heat-treated C70 nanotubes, though the peak heights became smaller by the heat treatment. The retained C70 molecules in the heat-treated tubes can be confirmed also by a HRTEM observation shown later.

Fig. 7 shows an example of heat-treated C70 nanotube with a length of 50 μm, an outer diameter of 475 nm and an inner diameter of 239 nm. As shown in the enlarged image of Fig. 8, the through-hole tubular structure could be retained after the heat treatment in air.

Fig. 9 shows a HRTEM image and its FFT pattern for the heat-treated C70 nanotube. By analyzing five FFT patterns for the HRTEM images including Fig. 9, the lattice-plane spacings of heat-treated C70 nanotube are calculated as shown in Table 1.

Since, the d-spacings of the C70 nanotubes shown in Table 1 are close to those of the orthorhombic structure ‘Orth II’ proposed by Oh et al. [15], the lattice constants \(a\), \(b\) and \(c\) were estimated from the (2 2 0) and (0 0 2) plane spacings, assuming orthorhombic structures.

The orthorhombic structures in Table 1 that are derived from the HRTEM-FFT patterns are different from the fcc structure of C70 nanotubes that is derived from their XRD measurement [11]. It is conjectured that the crystal structure
of the C\textsubscript{70} nanotube was distorted from the initial fcc structure by irradiation of high-energy electron beam and became closer to the orthorhombic structure through an orientational ordering of C\textsubscript{70} molecules.

The averaged center-to-center distance ($D$) of C\textsubscript{70} molecules along the tube growth axis can be calculated from the (2 2 0) lattice plane spacings and shown in Table 1. It is found that all the C\textsubscript{70} nanotubes have similar $D$ values that are close to the value of $D\ast = 1.03$ nm of the C\textsubscript{70} molecules which are densely packed along a [1 1 0] direction of Orth II phase. This fact shows that the C\textsubscript{70} molecules are densely packed along the [1 1 0] tube growth axis without having impurity elements between adjoining C\textsubscript{70} molecules.

Table 1 also shows the primitive unit cell volume ($V_p$) for the C\textsubscript{70} nanotubes and the Orth II phase. The $V_p$ value of the as-prepared C\textsubscript{70} nanotube (Fig. 2) is about 5\% greater than that of the heat-treated C\textsubscript{70} nanotube (Fig. 7) and the Orth II phase. This unit cell volume expansion in the as-prepared C\textsubscript{70} nanotubes indicates that impurity solvent molecules are contained in them. It is found that the heat treatment in air for the C\textsubscript{70} nanotubes is effective to remove the contained solvent molecules. This method may be utilized as a convenient purification technique for practical applications.

Fig. 5. (a) HRTEM image for the C\textsubscript{70} nanotube of Fig. 2, and (b) FFT pattern for the enclosed part of photo (a).

Fig. 6. FT-IR spectra for (a) the heat-treated C\textsubscript{70} nanotubes, (b) as-prepared C\textsubscript{70} nanotubes fabricated by use of IPA and pyridine; and (c) pure C\textsubscript{70} powder.

Fig. 7. TEM image of a C\textsubscript{70} nanotube annealed in air at 250 °C for 4 h.

Fig. 8. Enlarged TEM image for the left end of the heat-treated C\textsubscript{70} nanotube of Fig. 7.
shrinkage of inside solvated matrix during the heat treatment. It is assumed that the solvated inside cores of initially formed C70 nanowhiskers are soft and redissolved into the solution to form the tubular structure of C70. This observation suggests that the key point to prepare the C70 nanotubes is to obtain the C70 nanowhiskers with a core-shell structure that has an insoluble surface layer and an inside core soluble to organic solvents. For the moment, the C70 nanotubes are assumed to be formed by this core dissolution mechanism.

The TEM image of Fig. 11(a) shows a C70 nanotube heat-treated at 1100°C with 410 nm in outer diameter and 260 nm in inner diameter. The averaged wall thickness is 75 nm, which is much smaller than the wall thickness of the as-prepared C70 nanotubes, indicating a reduction in wall thickness by the heat treatment. The SAEDP of Fig. 11 (b) shows that the crystalline wall was turned amorphous by the heat treatment. Since, the amorphous carbon wall has a porous structure, the heat-treated C70 nanotubes should have a high specific surface area and may be applicable for the platinum catalyst carriers for polymer electrolyte fuel cells. The formation of amorphous carbon wall from C70 nanotubes is not obvious, since it is known that C70 evaporates by heating under a low pressure [17]. The amorphous nano carbon tube of Fig. 11 is a kind of ‘fullerene shell tubes’ that were previously reported [8]. This result demonstrates an easy method to prepare the fullerene shell tubes.

4. Conclusions

As shown above, the LLIP method is a powerful technique to prepare the nanotubes composed of C70 molecules.

The present research can be summarized as follows.

(1) C70 nanotubes have been successfully prepared by use of isobutyl alcohol as well as isopropyl alcohol by the liquid–liquid interfacial precipitation method.
(2) The wall of C70 nanotubes has a laminar structure with C70 molecules close-packed along the [1 1 0] tube growth axis.
(3) The heat-treated (in air) C70 nanotubes have showed a unit cell volume smaller than the as-prepared C70 nanotubes. The heat treatment in air is effective to remove the contained impurity solvent molecules in the C70 nanotubes.
(4) The C70 nanotubes have became amorphous nano carbon tubes (‘fullerene shell tubes’) by heating at high temperature in vacuum, and a reduction in wall thickness was observed.

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References

[1] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (6348) (1991) 56.
[2] H. Nishino, C. Yamaguchi, H. Nakaoka, R. Nishida, Carbon nanotube with amorphous carbon wall: α-CNT, Carbon 41 (2003) 2165–2167.
[3] K. Miyazawa, Y. Kuwasaki, A. Obayashi, M. Kuwabara, C60 nanowhiskers formed by the liquid–liquid interfacial precipitation method, J. Mater. Res. 17 (2002) 83–88.
[4] K. Miyazawa, C_{60} nanowhiskers fabricated by forming liquid/liquid interfaces in the systems of toluene solution of C_{60} and isopropyl alcohol, J. Am. Ceram. Soc. 85 (2002) 1297–1299.

[5] K. Miyazawa, T. Mashino, T. Suga, Structural characterization of the C_{60}(C(COOCH_3))_2 whiskers prepared by the liquid–liquid interfacial precipitation method, J. Mater. Res. 18 (2003) 2730–2735.

[6] M. Tachibana, K. Kobayashi, T. Uchida, K. Kojima, M. Tanimura, K. Miyazawa, Photo-assisted growth and polymerization of C_{60} ‘nano’ whiskers, Chem. Phys. Lett. 374 (2003) 279–285.

[7] K. Miyazawa, T. Mashino, T. Suga, Liquid phase synthesis of the nanowhiskers of fullerene derivatives, Trans. Mater. Res. Soc. Jpn 29 (2004) 537–540.

[8] K. Miyazawa, T. Suga, Transmission electron microscopy investigation of fullerene nanowhiskers and needle-like precipitates formed by using C_{60} and (n^2-C_{60})Pt(PPh_3)_2, J. Mater. Res. 19 (2004) 2410–2414.

[9] K. Miyazawa, T. Suga, Transmission electron microscopy investigation of tubular and capsular needlelike crystals of C_{60} produced by the liquid–liquid interfacial precipitation method, J. Mater. Res. 19 (2004) 3145–3148.

[10] H. Sakuma, M. Tachibana, H. Sugiura, K. Kojima, S. Ito, T. Sekiguchi, Y. Achiha, Growth and structures of C_{60} shells, J. Mater. Res. 12 (1997) 1545–1550.

[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 (2005) 688–695.

[12] A.R. McGhie, J.E. Fischer, P.A. Heiney, P.W. Stephens, R.L. Cappeletti, D.A. Neumann, W.H. Mueller, H. Mohn, H-U. ter Meer, Phase transitions in solid C_{70}: supercooling, metastable phases, and impurity effect, Phys. Rev. B 49 (1994) 12614–12618.

[13] H.S. Chen, A.R. Kortan, R.C. Haddon, D.A. Fleming, Thermodynamics of C_{60} in pure O_2, N_2 and Ar, J. Phys. Chem. 96 (1992) 1016–1018.

[14] K. Miyazawa, K. Hamamoto, S. Nagata, T. Suga, Structural investigation of the C_{60}/C_{70} whiskers fabricated by forming liquid–liquid interfaces of toluene with dissolved C_{60}/C_{70} and isopropyl alcohol, J. Mater. Res. 18 (2003) 1096–1103.

[15] D.H. Oh, Y.H. Lee, Orientational ordering of solid C_{70}, Phys. Rev. Lett. 75 (1995) 4230–4234.

[16] K. Miyazawa, J. Minato, H. Zhou, T. Taguchi, I. Homma, T. Suga, Structure and electrical properties of heat-treated fullerene nanowhiskers as potential energy device materials. J. Eur. Ceram. Soc., in press [doi: 10.1016/eurceramsoc.2005.07.010].

[17] W.B. Zhao, Z.D. Zhang, Z.Y. Ye, J.L. Zhang, C.Y. Li, D.L. Yin, Epitaxial thin films of C_{70}, growth and structure characterization, Solid State Commun. 85 (1993) 311–315.