

Structural characterization of room-temperature synthesized fullerene nanowhiskers

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Abstract Structural properties of various kinds of room-temperature synthesized C_{60} fullerene nanowhiskers were investigated by TEM and XRD. The C_{60} nanowhiskers prepared by use of toluene lost their initial solvated hexagonal structure faster than the C_{60} nanowhiskers prepared by use of *m*-xylene. The hexagonal structure of C_{60} nanowhiskers prepared by use of toluene was stabilized by adding $C_{60}[C(COOC_2H_5)_2]$. These results suggest that large solute molecules in the C_{60} nanowhisiker matrix stabilize their initially solvated hexagonal structure. Furthermore, the addition of a sufficient amount of C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine) into the *m*-xylene solution of C_{60} produced the C_{60} nanowhiskers indicating the formation of ordered solid solution of C_{60} and C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine).

Key words carbon • C_{60} • fullerene • nanowhisiker • structure • TEM

Introduction

Since the discovery of C_{60} in 1985 [3], a variety forms of solution grown C_{60} needle-like crystals with diameters of the order of micrometers ~ ten micrometers have been reported [1, 4, 13, 16]. Contrary to these thick needle-like crystals of C_{60} , various new forms of thin whiskers composed of C_{60} and C_{70} fullerene molecules or C_{60} derivative molecules, “fullerene nanowhiskers”, have been successfully produced by the liquid-liquid interfacial precipitation method (LLIP method) [7–9]. It has been shown that the C_{60} nanowhiskers are single crystalline, have submicrometer diameters and grow to hundred micrometers ~ millimeter order in length [8, 15].

We have shown that not only the solid nanowhiskers, but also tubular nanowhiskers, “fullerene nanotubes”, composed of fullerene molecules can be prepared by the LLIP method by using pyridine solutions of fullerenes and isopropyl alcohol (IPA) [6, 10, 11]. We can call the fullerene nanowhiskers and fullerene nanotubes “fullerene nanofibers” as well. Thus, the fullerene nanofibers have two kinds of solid and tubular morphologies.

In our first paper, X-ray diffraction (XRD) experiments showed that the C_{60} nanowhiskers prepared by use of the toluene-IPA system and dried at room temperature had a face-centered cubic (fcc) structure [8]. However, we recently found that the as-prepared C_{60} nanowhiskers had a solvated crystal structure whose lattice constants could be fitted by the hexagonal structure model proposed by Ramm *et al.* [5, 14]. Further, it was shown that the initially solvated structure of C_{60} nanowhiskers turned to the fcc structure through the evaporation of contained solvents [5]. It was also

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shown that the solvated crystal structure of C_{60} nanowhiskers prepared by use of toluene turned to the cubic structure faster than the C_{60} nanowhiskers prepared by use of *m*-xylene [5]. In the present paper, we are going to examine this phenomenon more minutely.

The LLIP method can form various alloys of C_{60} and C_{60} derivatives. Also, it is indicated that the solvated structure of C_{60} nanowhiskers can be stabilized by adding C_{60} derivative molecules. In this paper, the authors examine the influence of impurity solvent and C_{60} derivative molecules on the structural stability of C_{60} nanowhiskers using X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis techniques.

Experimental

The fullerene nanowhiskers were prepared by the LLIP method [8]. The starting material is a toluene or *m*-xylene solution saturated with as-received C_{60} powder (99.5%, MTR Ltd., Cleveland, OH, USA). To form an interface between the C_{60} saturated toluene or *m*-xylene solution and isopropyl alcohol (IPA), IPA was gently added to the aforementioned solution with fixed concentration in a transparent glass bottle. This process was performed at a temperature of $15^{\circ}\text{C} \sim 20^{\circ}\text{C}$ and the glass bottle was stored at 20°C for about ten days in an incubator with a transparent plastic window (SANYO MIR-153, SANYO Electric Co. Ltd., Japan) to grow the C_{60} nanowhiskers.

Mixed fullerene powders with compositions of (a) $C_{60} - 4.1 \text{ mol}\% C_{60}[\text{C}(\text{COOC}_2\text{H}_5)_2]$, (b) $C_{60} - 21 \text{ mol}\% C_{60}[\text{C}(\text{COOC}_2\text{H}_5)_2]$, (c) $C_{60} - 7.8 \text{ mol}\% C_{60}(\text{2-methoxycarbonyl-}N\text{-methylpyrrolidine})_2$ and (d) $C_{60} - 18 \text{ mol}\% C_{60}(\text{2-methoxycarbonyl-}N\text{-methylpyrrolidine})$ were prepared. These C_{60} derivatives were synthesized at

Kyoritsu College University. Toluene was used as the solvent for powder (a), while *m*-xylene was used for powders (b), (c) and (d). The LLIP method was applied for preparation of the fullerene nanowhiskers prepared from these mixed powders. The various C_{60} nanowhiskers were similarly grown in this process. The composition of the whiskers prepared using powder (a) was analyzed by high pressure liquid chromatography (HPLC) for the sample redissolved into toluene.

The structure of C_{60} nanowhiskers was characterized by XRD ($\text{CuK}\alpha$ radiation, RINT 2000, Rigaku Corporation, Japan) and HRTEM (JEM-4010, 400 kV, JEOL, Japan). More than five fast Fourier transform (FFT) patterns were analyzed to determine the lattice plane spacings when the HRTEM images were used for the crystal structure analysis.

Results and discussion

Characterization of C_{60} nanowhiskers prepared by use of *m*-xylene and IPA

The C_{60} nanowhiskers prepared by use of *m*-xylene and IPA in the present experiment exhibited red brownish color. The XRD profiles for these C_{60} nanowhiskers are shown in Fig. 1. Figure 1a shows an XRD profile for the sample dried at room temperature in air for 60 min after sampling from a bottle, and Fig. 1b shows an XRD profile for the sample dried for nine days at room temperature in air. Those XRD peaks were indexed referring to the hexagonal model proposed by Ramm *et al.* for the crystals of $C_{60} \cdot 2\text{C}_8\text{H}_{10}$ that were prepared by the cocrystallization of C_{60} with xylene [14]. All the XRD peaks shown in Fig. 1a could be indexed by a hexagonal system (h) with the lattice constants with $a = 2.411 \text{ nm}$ and $c = 1.045 \text{ nm}$, where the c -axis is set

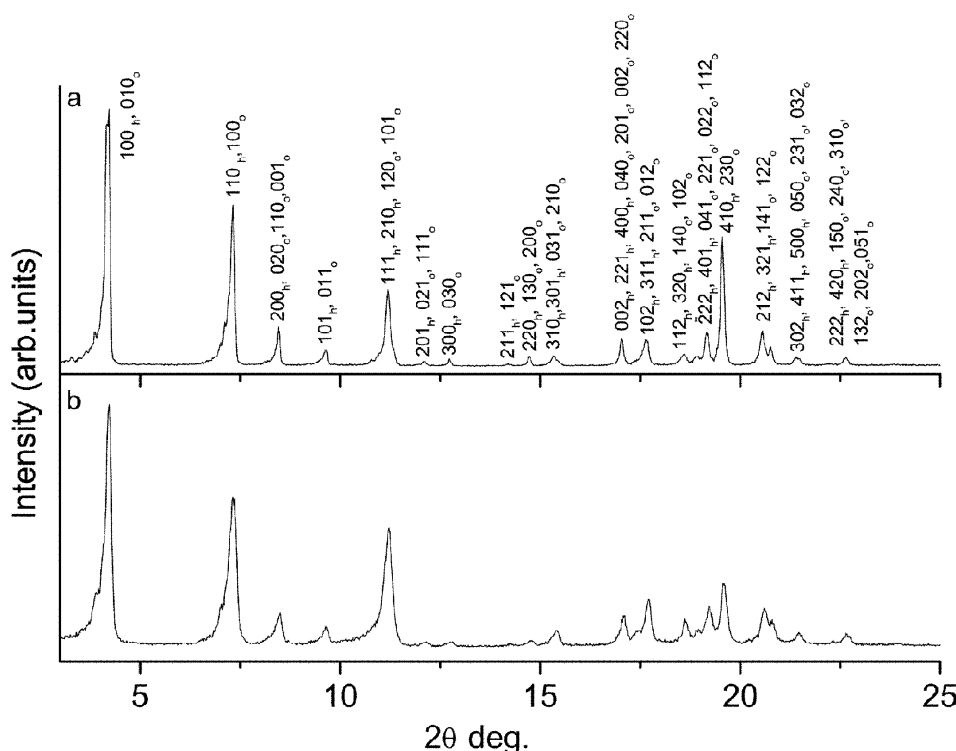


Fig. 1. XRD profiles for the C_{60} nanowhiskers prepared by use of *m*-xylene and IPA. (a) XRD profile taken 60 min after sampling from the glass bottle. (b) XRD profile taken 9 days after the sampling.

to be parallel to the whisker growth axis as shown in the following TEM observations. The 101_h peak which could not be observed in our previous work [5] has been indexed in the present research.

The XRD peaks, however, can also be indexed by assuming a body-centered orthorhombic (bco) lattice (o) with lattice constants $a = 1.208$ nm, $b = 2.094$ nm and $c = 1.045$ nm, as shown in the same figure. This solvated structure was stable after nine days' drying at room temperature in air, as shown in Fig. 1b, which can be indexed by the hexagonal system with lattice constants $a = 2.396$ nm and $c = 1.040$ nm, or by the bco lattice with lattice constants $a = 1.201$ nm, $b = 2.094$ nm and $c = 1.040$ nm. The XRD peaks of Fig. 1b became broader than those of Fig. 1a, showing that disordering in the structure occurred. This disordering is supposed to have been caused by evaporation of solvent molecules stabilizing the hexagonal structure.

A unit cell model to explain the above hexagonal structure has been constructed according to the model of Ramm *et al.* [14] as shown in Fig. 2, where the C_{60} molecules are shown by the spheres with van der Waals radius of $r_0 (= c/2)$. The whisker growth axis is parallel to the c -axis of close-packed direction of C_{60} molecules.

As shown above, the initially solvated C_{60} nanowhiskers have two possible crystal structures of hexagonal and orthorhombic systems. On the other hand, Kobayashi *et al.* recently showed that most of the cross-sectioned surfaces of the C_{60} nanowhiskers prepared by them had hexagonal shapes [2]. Although this morphological observation does not guarantee the hexagonal crystal system of the C_{60} nanowhiskers, in the present research, the XRD patterns and the results

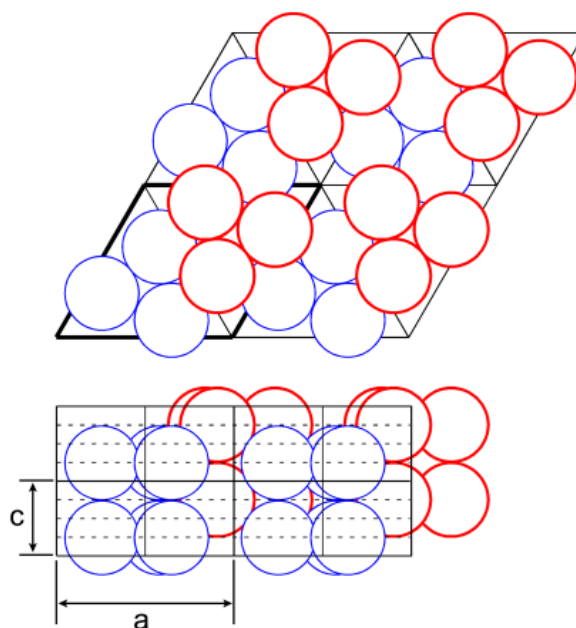


Fig. 2. Unit cell model for the hexagonal C_{60} nanowhiskers that was constructed according to the hexagonal unit cell of solvated C_{60} proposed by Ramm *et al.* [14].

of TEM observations on the solvated crystal structure of C_{60} nanowhiskers are indexed assuming the hexagonal crystal system in order to avoid confusion.

TEM observations were done for the structure refinement of C_{60} nanowhiskers prepared by use of *m*-xylene and IPA (Fig. 3a). The spots of selected area electron diffraction pattern (SAEDP, Fig. 3b) and fast

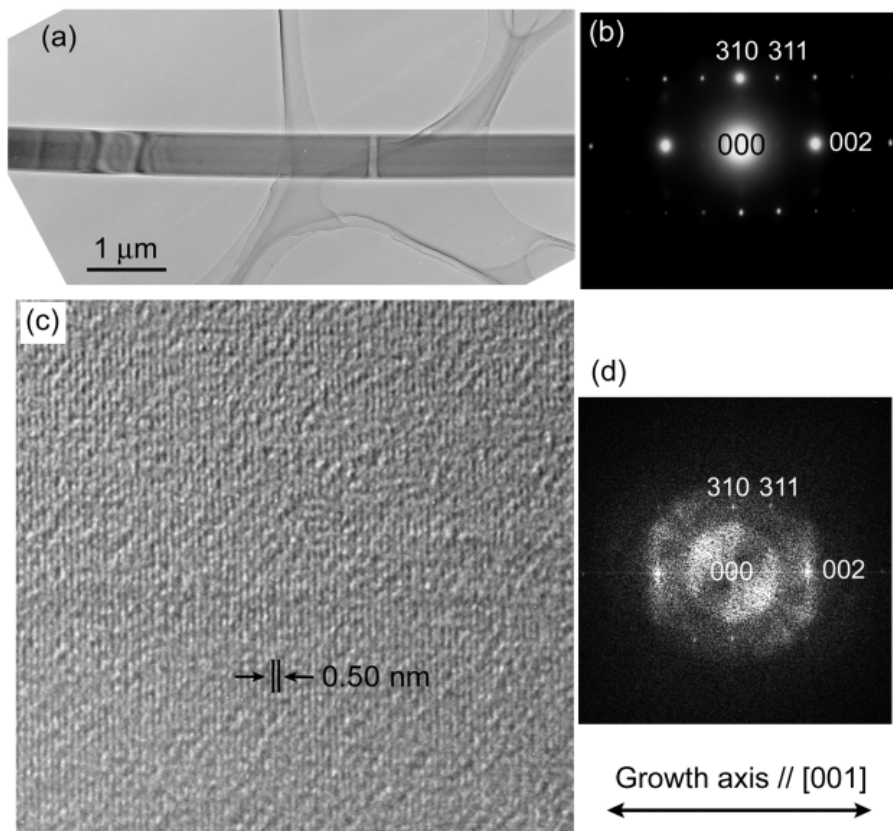


Fig. 3. (a) TEM image, (b) SAEDP and (c) HRTEM image for a C_{60} nanowhisker prepared by use of *m*-xylene and IPA. (d) FFT pattern for photo (c).

Fourier transform (FFT) pattern (Fig. 3d) for the HRTEM image of Fig. 3c were indexed by the hexagonal system. All the SAEDPs in the present paper were indexed by the hexagonal system, using both the lattice-plane spacings and interplanar angles. The HRTEM image, the FFT pattern and the corresponding SAEDP of Fig. 3 show that the C_{60} molecules are densely packed along the whisker growth axis which is parallel to the c -axis of the hexagonal system with a center-to-center distance (D) of 1.0 nm.

Structure refinement of C_{60} nanowhiskers prepared by use of toluene and IPA

Figure 4 shows the XRD profiles for the C_{60} nanowhiskers prepared by use of toluene and IPA. As shown in Fig. 4a, the C_{60} nanowhiskers which were dried for 40 min in air after sampling from a glass bottle showed the mixed phase of a hexagonal crystal structure with lattice constants of $a = 2.414$ nm and $c = 1.048$ nm, and a fcc structure with a lattice constant of $a = 1.425 \pm 0.003$ nm that is close to the lattice constant $a = 1.421 \pm 0.002$ nm of the as-received pure C_{60} powder (Fig. 4d). Although the hexagonal XRD profile of Fig. 4a can be

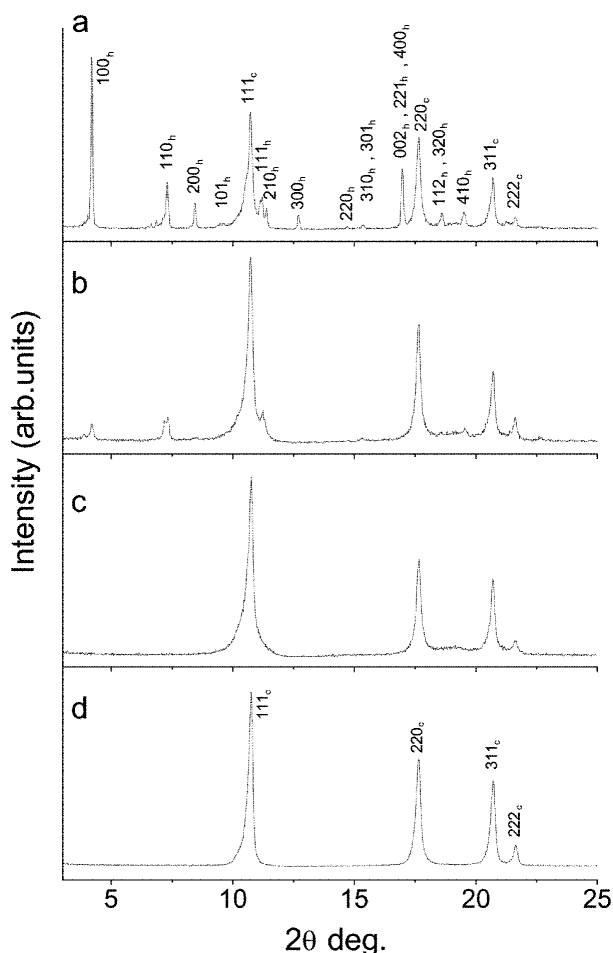


Fig. 4. XRD profiles for the C_{60} nanowhiskers prepared by use of a toluene solution of C_{60} and IPA. XRD profiles taken (a) 40 min after sampling from the glass bottle, (b) 90 min after the sampling, (c) 9 days after the sampling and (d) for pure C_{60} powder.

indexed by using an orthorhombic model with lattice constants of $a = 1.211$ nm, $b = 2.104$ nm and $c = 1.048$ nm as well, all the corresponding peaks were indexed by the hexagonal system as stated above.

As shown in Fig. 4b, the C_{60} nanowhiskers lost the initially solvated crystal structure quickly and most of them turned into the fcc structure after drying for 90 min, and completely turned into the fcc structure with a lattice constant of $a = 1.422 \pm 0.002$ nm nine days after the sampling (Fig. 4c). This result shows that the solvated structure of the C_{60} nanowhiskers prepared by use of toluene and IPA is unstable and turns to the cubic structure through evaporation of solvent molecules.

It has been found that the C_{60} nanowhiskers prepared by use of toluene lose their solvated structure faster than the C_{60} nanowhiskers prepared by use of *m*-xylene. This result shows that the solvated structure of C_{60} nanowhiskers is more stable when the solvent molecules are larger. This conjecture is confirmed again in the C_{60} nanowhiskers containing C_{60} derivatives like $C_{60}[C(COOC_2H_5)_2]$ as shown later. It is considered that the larger solvent molecules incorporated into the matrix of C_{60} nanowhiskers are more difficult to evaporate and make the solvated structure more stable at room temperature.

The transformation of the solvated hexagonal lattice to the fcc lattice must experience a drastic lattice reconstruction. It is considered that this lattice reconstruction is the reason why a high-density dislocations and stacking faults were introduced in the C_{60} nanowhiskers prepared by use of toluene and IPA in our previous research [7].

TEM investigation of the C_{60} nanowhiskers prepared by use of $C_{60} - C_{60}[C(COOC_2H_5)_2]$ two-component powders

The TEM image of Fig. 5a shows the C_{60} nanowhiskers prepared by use of the fullerene powder with a composition of $C_{60} - 4.1$ mol% $C_{60}[C(COOC_2H_5)_2]$, toluene and IPA. The C_{60} nanowhiskers are single crystalline, as can be seen in the SAEDP (c), and have a constant diameter along the whisker growth axis. An HPLC analysis of those whiskers revealed that the whiskers have a composition of $C_{60} - 4.2$ mol% $C_{60}[C(COOC_2H_5)_2]$. This analytical value is close to the used powder of $C_{60} - 4.1$ mol% $C_{60}[C(COOC_2H_5)_2]$. This result suggests that the $C_{60}[C(COOC_2H_5)_2]$ molecules formed a solid solution with the C_{60} molecules in the whiskers.

An HRTEM image for a $C_{60} - 4.2$ mol% $C_{60}[C(COOC_2H_5)_2]$ nanowhiskey of Fig. 5b was taken as shown in Fig. 6a where the surface of the whiskers is found to be smooth on an atomic scale. The hexagonal lattice parameters $a = 2.373 \pm 0.031$ nm and $c = 1.006 \pm 0.005$ nm were obtained by analyzing the HRTEM-FFT patterns including Fig. 6c. The structure image of Fig. 6b shows that the C_{60} cages are densely packed along the whisker growth axis with a center-to-center distance of 1.0 nm. The SAEDP of Fig. 5c well agrees with the FFT pattern of Fig. 6c.

As shown in the above XRD studies, the C_{60} nanowhiskers prepared by use of toluene and IPA turn

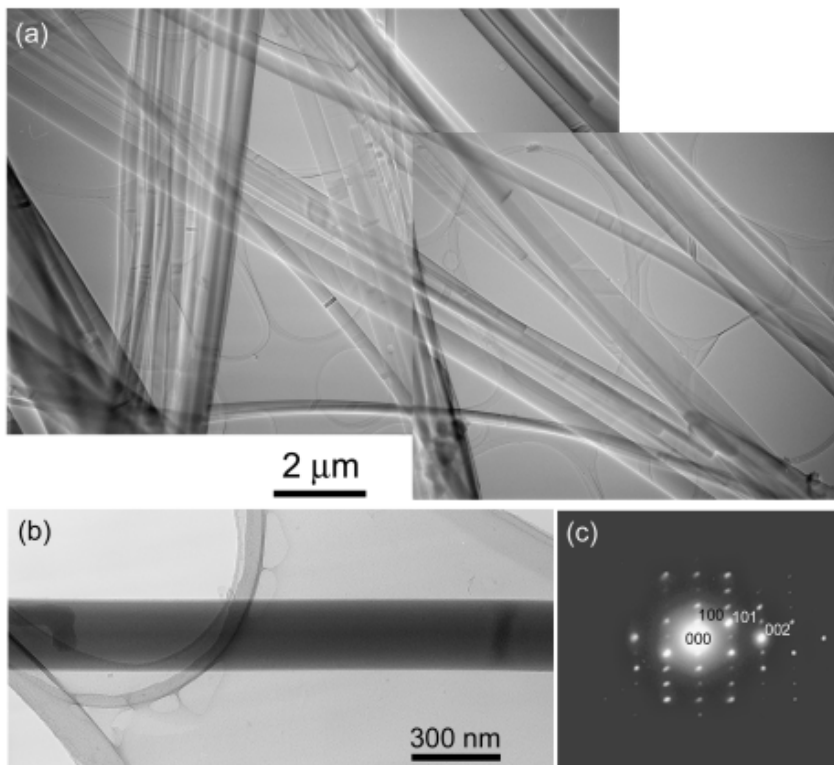


Fig. 5. (a) TEM image for the C_{60} nanowhiskers prepared by use of C_{60} – 4.1 mol% $C_{60}[C(COOC_2H_5)_2]$ powder, (b) TEM image for a part of C_{60} – 4.2 mol% $C_{60}[C(COOC_2H_5)_2]$ nanowhisker and (c) SAEDP indexed by the hexagonal system for the whisker (b).

to the cubic structure by the evaporation of contained solvent molecules. The C_{60} – 4.2 mol%

$C_{60}[C(COOC_2H_5)_2]$ nanowhiskers, however, retained their hexagonal structure even in the vacuum of TEM.

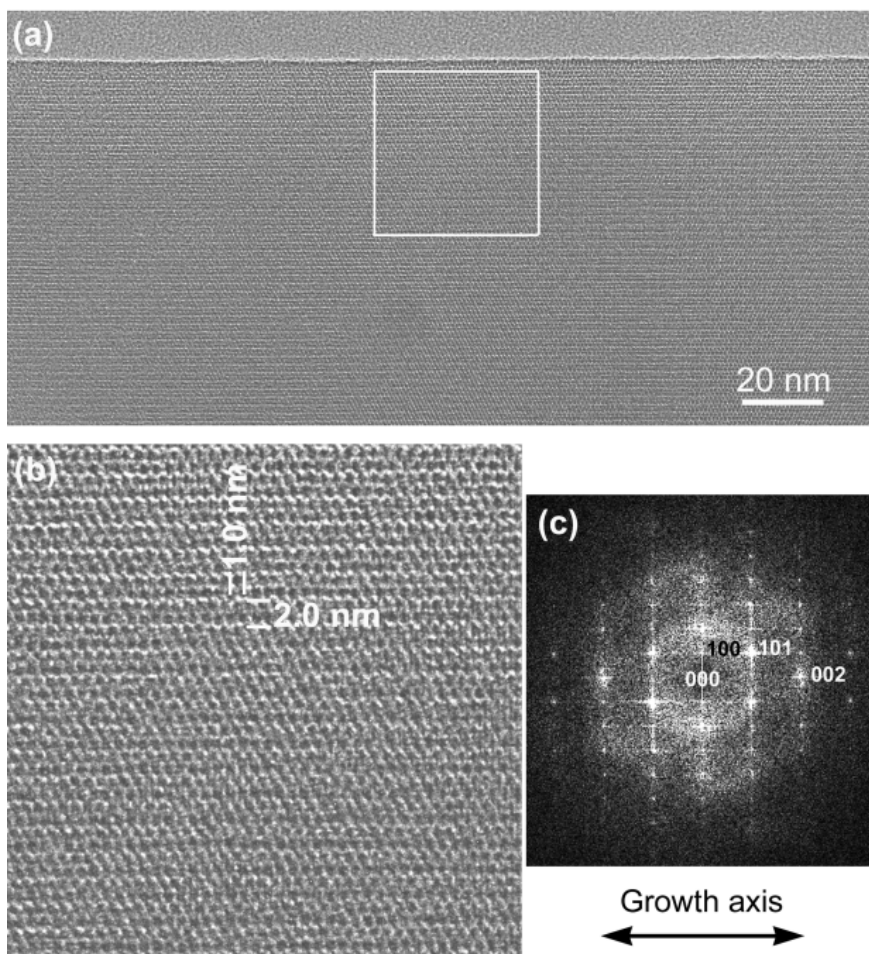


Fig. 6. (a) HRTEM image, (b) enlarged image for the area shown by the rectangle of photo (a), and (c) FFT pattern for photo (b) in the C_{60} – 4.2 mol% $C_{60}[C(COOC_2H_5)_2]$ nanowhisker of Fig. 5b.

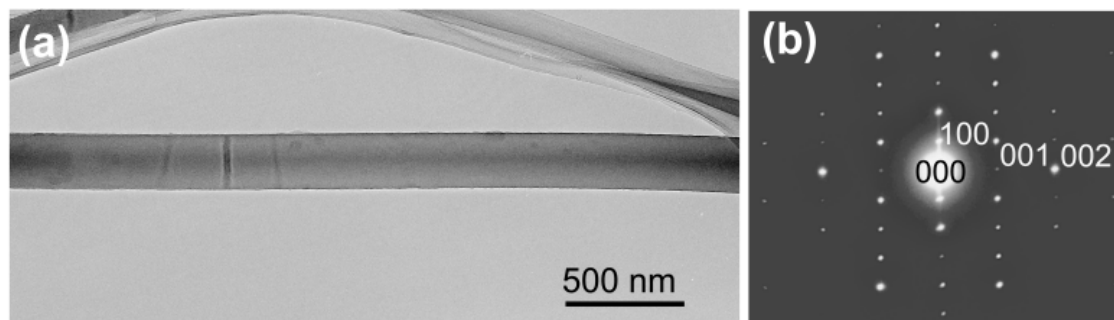


Fig. 7. (a) TEM image and (b) SAEDP for a part of C_{60} nanowhisker prepared using C_{60} – 21 mol% $C_{60}[C(COOC_2H_5)_2]$ powder.

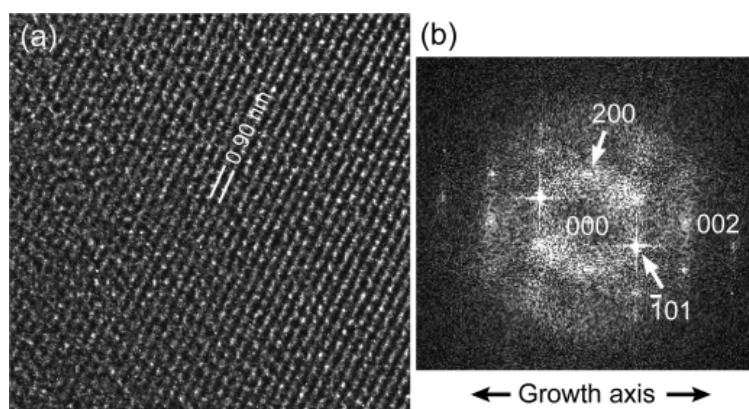


Fig. 8. (a) HRTEM image for a C_{60} nanowhisker prepared by use of C_{60} – 21 mol% $C_{60}[C(COOC_2H_5)_2]$ powder. (b) FFT pattern from photo (a).

This fact suggests that the solute $C_{60}[C(COOC_2H_5)_2]$ molecules stabilize the initially formed solvated crystal structure. This result further indicates that large molecules incorporated into the C_{60} nanowhisker matrix can stabilize the hexagonal structure. The large solute molecules must work as the impurity elements that obstruct dislocation motion and stabilize the hexagonal structure.

Figures 7 and 8 show TEM observations for the C_{60} nanowhiskers prepared by use of C_{60} – 21 mol% $C_{60}[C(COOC_2H_5)_2]$ powder. The SAEDP of Fig. 7b and the FFT pattern of Fig. 8b were indexed with a hexagonal system with lattice constants of $a = 2.351 \pm 0.075$ nm and $c = 1.009 \pm 0.009$ nm. These lattice constants well agree with those of the above C_{60} – 4.2 mol% $C_{60}[C(COOC_2H_5)_2]$ nanowhiskers and show no significant lattice expansion, although the C_{60} powder with a higher content of $C_{60}[C(COOC_2H_5)_2]$ was used in the present experiment. This fact suggests that the powder composition exceeded a solubility limit of $C_{60}[C(COOC_2H_5)_2]$ in the matrix of C_{60} nanowhiskers.

TEM investigation of the C_{60} nanowhiskers prepared by use of C_{60} (2-methoxycarbonyl-*N*-methyl-pyrrolidine) derivative of C_{60} two-component powders

As shown above, *m*-xylene and $C_{60}[C(COOC_2H_5)_2]$ can stabilize the initially formed solvated structure of C_{60} nanowhiskers.

The preparation of two-component whiskers was further tested using the powders of C_{60} – 7.8 mol% C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine)₂ (powder

A) and C_{60} – 18 mol% C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine) (powder B).

Figure 9 shows the C_{60} nanowhiskers prepared by using powder A. HRTEM observations were done for the whiskers, and an example of HRTEM image analysis is shown in Fig. 10. The spots of FFT pattern (Fig. 10c) were indexed by the hexagonal system with lattice constants of $a = 2.352 \pm 0.017$ nm and $c = 0.988 \pm 0.005$ nm. In this example, no strong hindrance of whisker growth was observed, although a small amount (2 ~ 3 mol%) of (η^2 - C_{60}) Pt(PPh_3)₂ addition hindered the whisker growth and formed short and porous

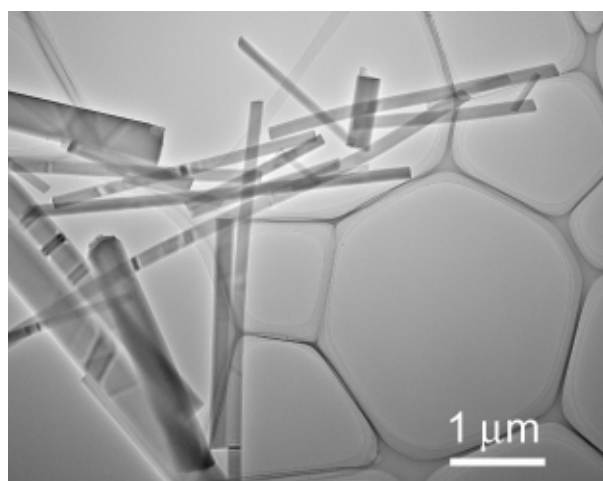


Fig. 9. TEM image for the C_{60} nanowhiskers prepared by use of C_{60} – 7.8 mol% C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine)₂ powder.

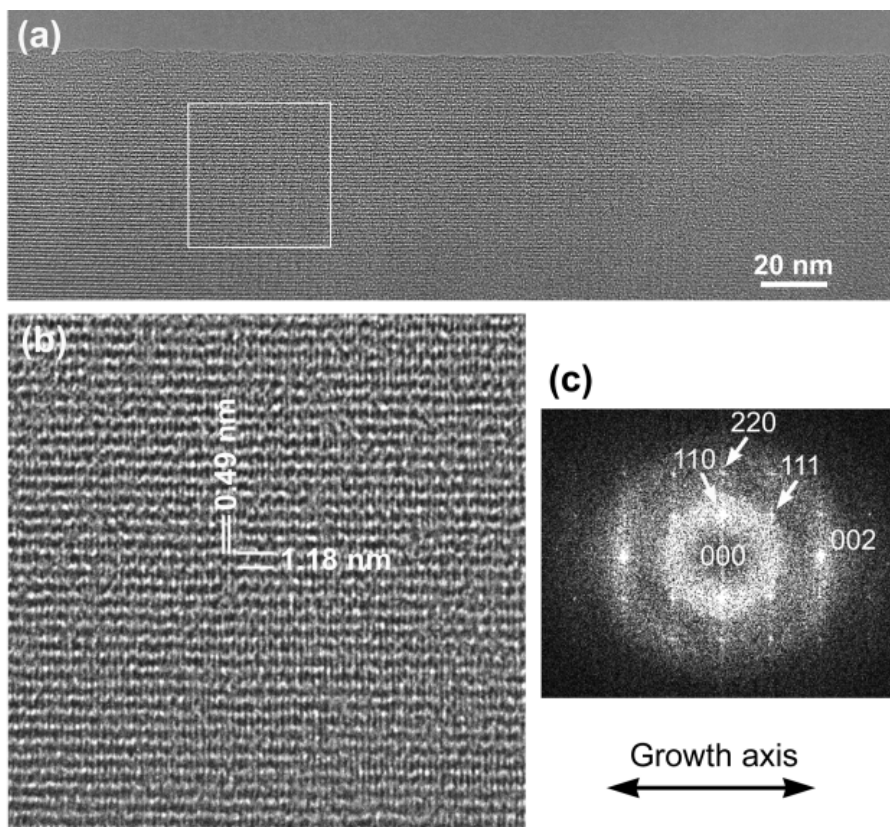


Fig. 10. (a) HRTEM observation for a C_{60} nanowhisker of Fig. 9 prepared by use of C_{60} - 7.8 mol% C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine)₂ powder, (b) magnified image for the area marked by the rectangle of photo (a), and (c) FFT pattern for photo (b).

tubular nanowhiskers of C_{60} [12]. Figure 11 shows a C_{60} nanowhisker prepared by use of powder B. The

continuous extinction fringes appearing in the marked places show the single crystallinity of the whisker.

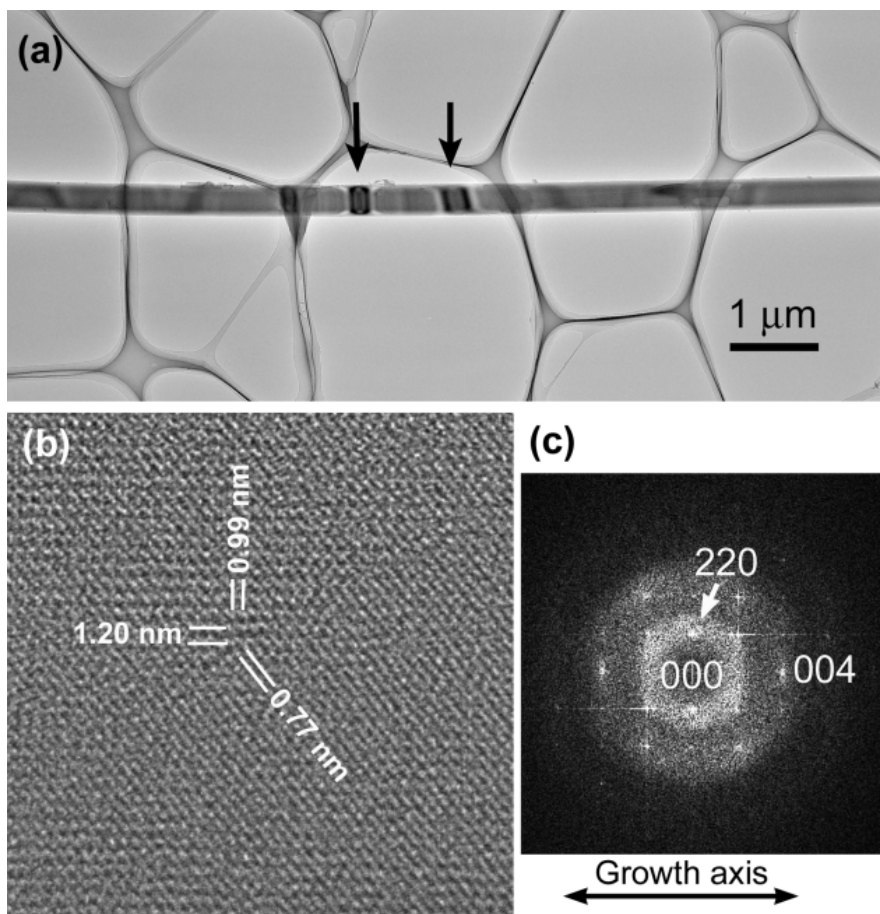


Fig. 11. (a) TEM image and (b) HRTEM image for a C_{60} nanowhisker prepared by use of the powder of C_{60} - 18 mol% C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine). (c) FFT pattern for photo (b).

Analyzing the FFT patterns including Fig. 11c and a few SAEDPs, the hexagonal lattice constants of $a = 4.817 \pm 0.039$ nm and $c = 1.977 \pm 0.027$ nm were obtained. This unit cell is larger just by a factor of two than the hexagonal unit cell of Fig. 2. This result shows the formation of ordered solid solution of C_{60} and C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine) and supports the incorporation of C_{60} derivative molecules into the matrix of C_{60} nanowhiskers. This example also suggests that various new phases of fullerene nanowhiskers can be obtained by combining different kinds of fullerene molecules.

In the future, those fullerene nanowhiskers will exhibit a variety of properties that depend on the species and composition of fullerene molecules, and will establish a new big field of fullerene science and technology.

Conclusion

The present research can be summarized as follows:

1. The C_{60} nanowhiskers prepared by use of toluene rapidly lost their solvated hexagonal structure and turned into a stable fcc structure during drying at room temperature, while the C_{60} nanowhiskers prepared by use of *m*-xylene retained their solvated hexagonal structure even after drying for nine days at room temperature.
2. The hexagonal structure of C_{60} nanowhiskers was made stable by the use of C_{60} powders containing C_{60} derivatives as well. It is suggested that the hexagonal structure of C_{60} nanowhiskers can be stabilized by the C_{60} derivative molecules incorporated into the matrix of C_{60} nanowhiskers.
3. The C_{60} nanowhiskers prepared by using the powder with a composition of $C_{60} - 18$ mol% C_{60} (2-methoxycarbonyl-*N*-methylpyrrolidine) showed a hexagonal unit cell indicating the formation of ordered solid solution of fullerenes.

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