Growth mechanism of vertically aligned fullerene microtubes prepared by the liquid-liquid interfacial precipitation method

S Toita1, K Miyazawa2, K Hotta2 and M Tachibana1

1Yokohama City University, Yokohama, 236-0027, Japan
2National Institute for Materials Science, Tsukuba, 305-0044, Japan

E-mail: toita.sho@nims.go.jp

Abstract. C60-based materials such as FNWs and FNTs are new candidates for organic electronics and solar cells. Recently, a method to produce vertically-aligned fullerene microtube crystals (VFMTs) has been established. The VFMTs are expected to be used as field emission devices, solar cells, fuel cells, and so forth. To realize such attractive applications, structures and arrangements of VFMTs should be controlled. In order to know the growth mechanism of VFMTs, Scanning electron microscopy (SEM) observations were performed for several injection periods of VFMTs. In the initial stage of synthesis (IPA injection time of 60 min), vertically aligned thin non-tubular fullerene microwhiskers (VFMWs) formed on AAO substrates. The outer and inner diameter of VFMWs became increased with increasing the injected amount of IPA. And also the size of tube holes became larger. The tubular structures appeared at an injection time of around 90 min. At an injection time of 120 min, vertically aligned FMTs with hexagonal cross sections and holes were obtained and their diameter and structure did not change up to the final stage of injection time of 300 min.

1. Introduction

Since C60 fullereone works as an efficient electron acceptor and has a relatively high electron mobility, C60-based materials are expected as promising candidates in fields of organic electronics and solar cells. It is known that C60 forms quasi one-dimensional single crystals such as FNWs (fullerene nanowhiskers [1,3]), tubular fullerene nanowhiskers (fullerene nanotubes: FNTs [2]) and relatively short fullerene nanowhiskers (fullerene nanorods [4]). “Fullerene nanorods” is an alias for short fullerene nanowhiskers. These materials are obtained by the liquid-liquid interfacial precipitation (LLIP) method [3]. An addition of isopropyl alcohol (IPA) to a C60-saturated toluene solution induces the nucleation and growth of C60 nano and micro whiskers. The order of addition can be changed in the LLIP method [7]. When we use pyridine in place of toluene, the products become C60 nanotubes.

Somani et al. performed organic thick film solar cell using short C60 nanowhiskers. To make more efficient organic solar cells (OSCs) using C60 materials, vertically aligned C60 whiskers must be more appropriate. Recently, Cha et al. succeeded to produce vertically aligned C60 microtubes (VFMTs) by modifying the LLIP method shown in ref. 3. In the method by Cha et al., an anodized alumina (AAO) membrane is set between the upper C60-saturated toluene solution and the lower IPA. When IPA is injected into the C60-toluene solution through the membrane from the lower side, V-FMTs form on the AAO substrates. C60-based materials with designed structures such as VFMTs are expected to be used in various applications. For example, field emission devices, solar cells, fuel cells, and so on.

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those applications can’t be realized without the design control of VFMTs and the detailed growth mechanism of VFMTs has to be clarified.

To understand the growth mechanism of VFMTs, we performed scanning electron microscopy (SEM) observation for the samples of several injection periods (injection time 60, 90, 120, 180 and 300 min).

![Schematic of synthesizing apparatus for VFMTs.](image)

**Figure 1.** Schematic of synthesizing apparatus for VFMTs.

### 2. Experimental

A schematic of synthesizing apparatus for VFMTs is shown in Fig.1. 3 mL of C$_{60}$-saturated toluene solution in a glass syringe was kept at 5 °C in an incubator. Then IPA was injected at a rate of 0.02 mL/min into the toluene solution through the membrane. Completely grown VFMTs were obtained when 300 min passed from the beginning of IPA injection. In this case, 6 mL of IPA was totally injected. Four injection periods of 60, 90, 120, and 180 min were adopted to observe the growth process of VFMTs. The amount of injected IPA for each injection time is shown in Table.1. The sample morphology was observed by a scanning electron microscope (JSM-6700F by JEOL). 100 samples were analyzed to obtain the average values of diameter, area of cross section and walls thickness.

The cross-sectional polygonal plane of a VFMT is approximated by a circle whose area is the same with the polygonal area. The outer and inner diameters of the VFMTs are calculated from the area of this circle. The wall thickness of VFMTs is calculated from the inner and outer diameters thus obtained.

| Injection time(min) | C$_{60}$-toluene solution (mL) | Injected IPA (mL) | Total solution volume of systems |
|---------------------|-------------------------------|------------------|---------------------------------|
| 60                  | 3.0                           | 1.2              | 4.2                             |
| 90                  | 3.0                           | 1.8              | 4.8                             |
| 120                 | 3.0                           | 2.4              | 5.4                             |
| 180                 | 3.0                           | 3.6              | 6.6                             |
| 300                 | 3.0                           | 6.0              | 9.0                             |

### 3. Results and discussion

SEM images for samples in the initial injection period (injection time 60 min) are shown in Fig.2. Vertically aligned thin fullerenes micro non-tubular whiskers formed on a AAO membrane. All the prepared samples exhibited various morphologies with different diameters and lengths.
The typical cross-sectional shapes of VFMWs are shown in Figs. 2(a)-(c). In the observed 100 samples, about 61 VFMWs had no holes on their top surface like Fig. 3(a). 13 of the VFMWs had small holes as shown in Fig. 2(b). The diameter of this type of VFMWs is less than 300 nm. The other VFMWs had larger holes (500 nm ~ 2.62 μm) (Fig. 2(c)). The classification criteria for the morphological types of VFMWs are shown in Table 2.

**Table 2. Classification criteria for the morphological types of VFMWs for the injection time of 60 min.**

| Type (a) | Type (b) | Type (c) | Others |
|----------|----------|----------|--------|
| Hole shape approximation | No hole | Circle | Circle | - |
| Inner diameter | 0 μm | ~ 0.3 μm | 0.3 ~ 2 μm | - |

The “Abundance of sample type [%]” is defined as follows.

\[
\text{Abundance of sample type} = \frac{\text{The number of the same type samples}}{\text{The total number of observed samples}} \times 100 \, [%]
\]

The ratio of hole area to the cross-sectional area in VFMWs is calculated as follows.

\[
\text{Hole area ratio} = \frac{\text{Area of hole} \, [\mu m^2]}{\text{Area of cross section} \, [\mu m^2]} \times 100 \, [%]
\]

The average percentage of hole area was only 1.49 % of the total cross-sectional area of VFMWs. This means that most of the VFMWs formed in the initial injection period have the non-tubular morphology. The average diameter at an injection time of 60 min was 6.15 μm.

![Figure 2. SEM images of VFMWs (injection time 60 min). (a)-(c) typical cross sections of VFMWs for an injection time of 60 min. (a) VFMW without hole, (b) VFMW with a small hole, (c) VFMW with a relatively large hole. (d) Inner hole diameter distribution of VFMWs. (e) Plan view and (f) inclined view of VFMWs by SEM.](image)

The diameter of VFMWs increased with increasing the amount of injected IPA. The tubular structures appeared at an injection time of around 90 min for diameters greater than a certain value (Fig. 3). All the tubes showed regular hexagons, but their tube holes were not hexagonal. The holes can

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be classified into 3 types of morphologies. 24% of the VFMTs had such irregular shapes as shown in Fig.3(a), where various shapes of holes like circular, trigonal, pentagonal forms and so forth were observed. And their ratio of hole area against the area of cross-section was less than 10%.

The most typical tube structure is shown in Fig.3(b). The VFMTs show the incomplete hexagonal holes with surrounding terraces. The average inner diameter of VFMTs like Fig.3(b) was less than 10 \( \mu m \). 10% of them had relatively large holes whose inner diameter was more than 10 \( \mu m \) (Fig.3(c)). Non-tubular whiskers like Fig.2(a) or VFMWs with small circular holes like Fig.2(b) are also observed.

There is a correlation between the value of inner diameter and the hole shape. The more inner diameter becomes larger, the more hole shape becomes closer to hexagonal. This correlation was also observed in the whole injection periods. The classification criteria for the morphological types for the injection time of 90 min are shown in Table 3.

Table 3. Classification criteria for the morphological types of VFMTs for the injection time of 90 min.

| Type (a)          | Type (b)          | Type (c)          | Others                  |
|-------------------|-------------------|-------------------|-------------------------|
| Hole shape        | Irregularly shaped polygons | Imperfect hexagon | Imperfect hexagon | No hole or small circular hole |
| approximation     |                   |                   |                         |
| Inner diameter    | 2 ~ 5 \( \mu m \) | 5 ~ 10 \( \mu m \) | 10 ~ 20 \( \mu m \)    | 0 ~ 2 \( \mu m \)               |

In this injection period, the average ratio of hole area to the cross-sectional area was about 17% and the average diameter was 15.7 \( \mu m \).

![Typical cross-sectional SEM images](image)

Figure 3. Typical cross-sectional SEM images (a, b, c, e, f) of VFMTs for the injection time of 90 min (a) VFMT with an irregularly shaped hole, (b) VFMT with an imperfect hexagonal hole and (c) VFMT with relatively large hole. (d) Inner diameter distribution of VFMTs. (e) Plan view and (f) inclined view of the VFMTs by SEM.

The VFMTs with hexagonal cross sections and holes were obtained for an injection time of 120 min. These structures were almost the same as the final products of the injection time of 300 min (Fig.5). In this injection period, 92% of them had the hexagonal cross sections and tube holes as shown in Figs.4(a) and (b). But the rest of 5% had imperfect hexagonal holes with wavy sides like Fig.4(c).
In the sample as shown in Fig.4(b), the shape of hole has a hexagonal symmetry and the tube wall is thin, while the sample shown in Fig.4(a) has a thicker tube wall without the hexagonal symmetry. It is found that the shape of holes approaches regular hexagons with decreasing the wall thickness. The classification criteria for morphological types for the injection time of 120 min are shown in Table 4.

Table 4. Classification criteria for the morphological types of VFMTs for the injection time of 120 min.

| Hole shape approximation | Type (a)          | Type (b)          | Others               |
|--------------------------|-------------------|-------------------|----------------------|
|                          | Incomplete hexagon| Regular hexagon   | Other polygons or irregularly shaped holes |
| Wall thickness           | 4.5 μm ~ 5.5 μm   | 3.5 ~ 4.5 μm      | 5.5 ~ 6.5 μm         |

The average ratio of hole area to the cross-sectional area was about 44 %. And the average outer diameters for the injection time of 120 min and 180 min were 28.4 μm and 28.8 μm, respectively.

No significant difference was observed between the samples for the injection time of 120 min and those for the injection time of 180 min.

![Figure 4. Typical cross-sectional SEM images (a, b, c, e, f) of VFMTs for the injection time of 120 min.](image)

- (a) VFMT with an incomplete hexagonal hole
- (b) VFMT with a regular hexagonal hole
- (c) an example for other polygonal holes
- (d) Inner diameter distribution of VFMTs
- (e) Plan view and (f) inclined view of VFMTs by SEM

![Figure 5. SEM images of the final products (injection time 300 min).](image)

- (a) Plan view
- (b) Inclined view of VFMTs
- (c) Cross-sectional view of a VFMT
- (d) Inner diameter distribution of VFMTs for the injected time 300 min
Fig. 6 shows the distribution of outer diameter of VFMTs for the different injection periods. The median of outer diameter for each period shifts to the right with increasing the injected amount of IPA. For the injection time of 120 min, the distribution of outer diameter became broader and showed the similar curves. The distribution of inner diameter of VFMTs also showed the same behaviour.

![Figure 6. Outer diameter distribution of VFMTs measured as a function of injection time.](image)

4. Conclusion

It has been found that the vertically-aligned fullerene microtubes exhibit solid non-tubular structures in their initial injection period. At the injection time of 60 min, vertically aligned thin non-tubular C$_{60}$ whiskers formed on the AAO substrates. The ratio of the hole area to the cross-sectional area and the outer and inner diameters of the VFMWs increased with increasing the injection time.

The tubular structures appeared at the injection time of around 90 min. At the injection time of 120 min, vertically aligned FMTs with hexagonal cross sections were obtained and their morphology did not change up to the final stage of injection time of 300 min. This result shows that the formation of VFMTs completes within the injection time of 120 min.

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