Influence of the Solution Volume on the Growth of C₆₀ Nanowhiskers

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Abstract:

The lengths and diameters of C₆₀ nanowhiskers (C₆₀NWs) grown in solutions were investigated relative to the inner diameter of the glass bottle and the solution volume while maintaining the volumetric ratio of C₆₀-saturated toluene and isopropyl alcohol at 1:1. The mean lengths and diameters of the C₆₀NWs increased, and the distribution of the lengths and diameters broadened when increasing the solution volume. The mean crystal nucleus size of the C₆₀NWs was determined by analyzing the size dependence of C₆₀NWs on the solution volume. The lengths and diameters of C₆₀NWs asymptotically approach their upper limits when increasing the solution volume.

Keywords: A1. LLIP method; A1. Growth control; B1. C₆₀ nanowhisiker; B1. Fullerene nanowhisiker

1. Introduction

Fullerene nanowhiskers (FNWs) are thin, needle-like crystals composed of fullerene molecules, such as C₆₀, C₇₀, C₆₀[C(COOC₂H₅)₂], Sc₃N@C₈₀, and others [1, 2, 3, 4]. The needle-like fullerene crystals with diameters below 1000 nm are known as fullerene nanowhiskers [2, 3]. One-dimensional fullerene crystals are promising materials for optical, electrical and electronic devices, including superconductors [5, 6, 7, 8, 9], and controlling their size is essential. For example, the electrical resistivity of

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these materials decreases rapidly when decreasing the diameter of the C₆₀NWs [10, 11]. The photoluminescence peak for the C₆₀ microtubes shifts toward lower wavenumbers when decreasing their diameters [12]. Controlling the size of C₆₀NWs is also important during their mechanical applications because their Young's modulus changes relative to the diameter and aspect ratio (length/diameter) of the C₆₀NWs [13, 14, 15].

The growth of C₆₀NWs is influenced by the temperature, light, ratio of the poor solvent vs the good solvent for C₆₀, and concentration of water [16, 17, 18, 19, 22].

In our previous paper, the diameter of the C₆₀NWs was a linear function of the area of the liquid-liquid interface when the total volume of solvent is constant, while the inner diameter of glass bottle changes [20].

However, the length of the C₆₀NWs must also be controlled before any practical application. In the present paper, we will demonstrate how the length and diameter of C₆₀NWs change depending on the bottle size and the solution volume. These analytical results will elucidate the synthesis of C₆₀NWs with size control.

2. Experimental

A C₆₀-saturated toluene solution was prepared by dissolving C₆₀ powder (99.5 % MTR Ltd.) in toluene (non-dehydrated, Wako Pure Chemical Industries, Ltd., Osaka, Japan); the undissolved C₆₀ powder was removed via syringe filter with 450-nm pores (Puradisc TM, Whatman Inc., Clifton, USA).

The C₆₀NWs were synthesized through a modified LLIP method. Five differently sizes of transparent glass bottles were used, as shown in Fig. 1. For the LLIP method, a C₆₀-saturated toluene solution was poured into a glass bottle and an equal amount of isopropyl alcohol (IPA) was layered onto the C₆₀-saturated toluene solution. The glass bottle was capped and manually mixed by shaking the bottle 30 times in order to obtain homogeneous precipitation of embryo C₆₀ crystals [16]; afterwards, the bottles were stored in an incubator at 15 °C for 8 days to obtain well-grown C₆₀NWs, avoiding the

destabilization of C₆₀NWs by the impurity water contained in the solvents [19]. The synthesis of C₆₀NWs was repeated three times for each size of glass bottle. Table 1 shows the amount of C₆₀-saturated toluene solution and IPA with the sizes of the glass bottles.

The lengths and diameters of the C₆₀NWs were measured via scanning electron microscopy (SEM) (FIB-SEM Hitachi NB5000). In the SEM observations, all the C₆₀NWs were collected from the above three glass bottles with the same size and put into a glass bottle containing IPA. After a gentle manual mixing for homogenization, parts of the C₆₀NWs in the glass bottle were sampled onto a Si substrate for SEM observations. One hundred C₆₀NWs were visualized to measure their lengths and diameters using randomly selected SEM images.

3. Results and Discussion

As shown in Fig. 2, short and straight C₆₀NWs with uniform diameters along their growth axes were successfully synthesized in each glass bottle. In the SEM images, finer C₆₀NWs are observed when the bottle size decreases. Figs.3 and 4 show that the distributions of the length and diameter for the C₆₀NWs broaden when increasing the bottle size.

The mean lengths and diameters of the C₆₀NWs are plotted relative to the inner diameters of the bottles, as shown in Figs.5 and 6. The mean length and diameter are increased linearly when increasing the inner diameter of the glass bottle. The standard deviations for the length and inner diameter of C₆₀NWs increase, reflecting the broader distributions observed with the larger bottle sizes. Therefore, the uniformity of the C₆₀NWs depends on the size of the glass bottle and diverges when increasing the size of the glass bottle.

In addition, the length and diameter decrease when decreasing the bottle size. The y-intercepts are the smallest mean size of C₆₀NWs, which can be treated as the nucleus

for crystal growth; these particles should have a mean length of 2.1 μm and a mean diameter of 305 nm. The C_{60} nuclei should have an mean aspect ratio of 6.9 ($=2.1 \mu\text{m}/305 \text{ nm}$).

However, the aspect ratio for each C_{60}NW was calculated using the same data shown in Figs. 5 and 6. As shown in Fig. 7, the aspect ratio is observed to increase and broaden when increasing the inner diameter of the bottle. Fig. 8 shows the relationship between the mean aspect ratio and the inner diameter of the bottle. The smallest aspect ratio can be determined by using the y-intercept in Fig. 8; this value is 10.8. However, this value does not coincide with the value above (6.9). The large discrepancy between 10.8 and 6.9 in the aspect ratios indicates that the sizes of the C_{60}NW nuclei were estimated incorrectly, suggesting that the curve fittings were performed incorrectly. This result should have arisen from the fact that the above curve fittings were performed only for the bottle inner diameter and were not three-dimensionally performed. Therefore, analyses were also performed using the solution volumes, as shown in Figs. 9, 10 and 11. The solution volume is defined as the arithmetic sum of the C_{60} -saturated toluene solution and IPA (Table 1).

The length, diameter and aspect ratio of the C_{60}NW s were determined from the y-intercepts of Figs. 9, 10 and 11 are 5.02 μm , 387 nm and 13.1, respectively. The aspect ratio is 5.02 μm / 387 nm, producing an aspect ratio of 13.0. Because this value (13.0) is very close to 13.1, the size estimation using the solution volume must be correct. Therefore, the mean size of the C_{60}NW nuclei is estimated to be 5.02 μm long and 387 nm in diameter.

However, the fitted curves in Figs. 9 and 10 show that the mean length and diameter of C_{60}NW s approach the maximum values (16.6 μm and 784 nm, respectively). Therefore, the maximum mean size of the C_{60}NW s attained through the present synthetic method can be estimated from the data obtained after changing the solution volume.

Fig. 12 shows the relationship between the solution volume and the number of C₆₀NWs per unit volume (cm³) (= number density) formed in the glass bottles. The number of C₆₀NWs in each glass bottle was calculated using the mean size of the C₆₀NWs in the glass bottle and the quantity of C₆₀ powder dissolved in the glass bottle when using a saturated solution of C₆₀ in toluene (2.58 mg cm⁻³ at 15 °C [21]). The number density of the C₆₀NWs in solution decreases linearly when increasing the solution volume in the double logarithmic plot. The highest number of nuclei per unit volume of solution may be estimated from the crystal nucleus size calculated for the C₆₀NWs (5.02 μm long and 387 nm in diameter); this value is 1.3×10⁹ cm⁻³. The fitted curve ($y=1.12496 \times 10^9 / x^{0.5674}$) in Fig. 12 shows that the solution volume corresponding to the above number (1.3×10⁹ cm⁻³) is 0.77 cm³. Therefore, the smallest C₆₀NWs can be obtained when the solution volume is below 0.77 cm³ and when equal amounts of C₆₀-saturated toluene and IPA are used during the synthetic process.

However, the growth of C₆₀NWs changes depending not only on the solution volume but also on the combination of solvents used in the LLIP method. For example, tubular C₆₀NWs (C₆₀ nanotubes) with lengths longer than several millimeters were synthesized, using a LLIP method combined with ultrasonication and manual mixing, where 1 mL of C₆₀-saturated pyridine solution and 9 mL of IPA were used [23]. In this case, although the solution volume was 10 cm³, the length of C₆₀NWs far exceeds the size of the C₆₀NWs in the present experiment. Thus, in order to elucidate the growth mechanism of C₆₀NWs, how the combination of solvents influences the growth of C₆₀NWs is going to be investigated further more.

4. Conclusions

- (1) The mean lengths and diameters of C₆₀NWs increase when increasing the bottle size. However, the size distribution of the C₆₀NWs broadens for the length and diameter when increasing the bottle size.

- (2) The mean size of the C₆₀NW crystal nuclei can be determined from the y-intercepts for the mean diameters and lengths of the C₆₀NWs plotted versus the solution volume.
- (3) The mean lengths, diameters and aspect ratios for the C₆₀NWs asymptotically approach their upper limits when increasing the solution volume.
- (4) The number density of the C₆₀NWs in solution decreases when increasing the solution volume, revealing a linear relationship in their double logarithmic plot.
- (5) The minimum size of the C₆₀NWs should be synthesized when the solution volume is below 0.77 cm³.

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Figure captions

Table 1 Inner diameters of the glass bottles, and the amounts of C₆₀-saturated toluene solution and IPA used during the synthesis of the C₆₀NWs.

Fig. 1. Transparent glass bottles with inner diameters of (a) 10 mm, (b) 12.5 mm, (c) 18 mm, (d) 27 mm and (e) 36.5 mm, respectively.

Fig. 2. SEM images of the C₆₀NWs synthesized using glass bottles with inner diameters of (a) 10 mm, (b) 12.5 mm, (c) 18 mm, (d) 27 mm and (e) 36.5 mm.

Fig. 3. Length distribution of the C₆₀NWs synthesized using glass bottles with inner diameters of (a) 10 mm, (b) 12.5 mm, (c) 18 mm, (d) 27 mm and (e) 36.5 mm, respectively.

Fig. 4. Diameter distribution of the C₆₀NWs synthesized using glass bottles with inner diameters of (a) 10 mm, (b) 12.5 mm, (c) 18 mm, (d) 27 mm and (e) 36.5 mm, respectively.

Fig. 5. Mean lengths of the C₆₀NWs (y) plotted relative to the inner diameter of the bottle (x). The fitted curve equation is $y=0.397x + 2.1$.

Fig. 6. Mean diameters of the C₆₀NWs (y) plotted relative to the inner diameter of the bottle (x). The fitted curve equation is $y=12.9x + 305.4$.

Fig. 7. Aspect ratio distributions of the C₆₀NWs for bottles with inner diameters of (a) 10 mm, (b) 12.5 mm, (c) 18 mm, (d) 27 mm and (e) 36.5 mm, respectively.

Fig. 8. Relationship between the mean aspect ratio of the C₆₀NWs (y) and the inner diameter of the glass bottles (x). The equation for the fitted curve is $y=0.343x + 10.8$.

Fig. 9. Relationship between the solution volume (x) and the mean length of the C₆₀NWs (y). The equation for the fitted curve is $y= -11.6\exp(-x/18.7)+16.6$. The mean length asymptotically approaches 16.6 μm .

Fig. 10. Relationship between the solution volumes and the mean diameters of C₆₀NWs. The fitted curve equation is $y= -396.6\exp(-x/17.6) + 783.7$. The mean diameter approaches 784 nm asymptotically.

Fig. 11. Relationship between the solution volume (x) and the mean aspect ratio of the C₆₀NWs (y). The equation for the fitted curve is $y = -9 \exp(-x/14.2) + 22.1$. The mean aspect ratio approaches 22.1 asymptotically.

Fig. 12. Estimated number of C₆₀NWs per unit volume plotted versus the solution volume. The equation for the fitted curve is $y=1.12496 \times 10^9 / x^{0.5674}$.

Table 1 Inner diameters of the glass bottles, and the amounts of C₆₀-saturated toluene solution and IPA used during the synthesis of the C₆₀NWs.

Glass bottles (Fig.1)	Inner diameter (mm)	C ₆₀ -saturated toluene solution (cm ³)	IPA (cm ³)	Solution volume (cm ³)
(a)	10.0	0.75	0.75	1.5
(b)	12.5	1.5	1.5	3.0
(c)	18.0	4.0	4.0	8.0
(d)	27.0	10.0	10.0	20.0
(e)	36.5	40.0	40.0	80.0

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