Long-term Growth Investigation of C₆₀ Fullerene Nanowhiskers

Yumeno Akasaka and Kun'ichi Miyazawa

Fullerene Engineering Group, Exploratory Nanotechnology Research Laboratory,
National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0034, Japan
Fax: 81-29-860-4667, e-mail: AKASAKA.Yumeno@nims.go.jp, MIYAZAWA.Kunichi@nims.go.jp

C₆₀ nanowhiskers (C₆₀NWs) were synthesized by liquid-liquid interfacial precipitation method (LLIP method), using *m*-xylene as a good solvent solution of C₆₀ and isopropyl alcohol (IPA) as a poor solvent of C₆₀. The growth mechanism of C₆₀NWs was investigated by the long-term observations using optical microscopy. In the early stage of growth, C₆₀NWs grew faster and longer at 5 °C than at 20 °C. However as the growth time became longer, the growth rate of C₆₀NWs became greater at 20 °C than at 5 °C, and the longer C₆₀NWs were obtained at 20 °C than at 5 °C. Further, it is suggested that the growth of C₆₀NWs proceeds by repeating the dissolution and reprecipitation process of C₆₀NWs.

Key words: C₆₀ nanowhiskers, liquid-liquid interfacial precipitation method, LLIP method, fullerene

1. INTRODUCTION

In 1985, Kroto *et al.* discovered C₆₀ [1], and its physical and chemical properties and the applications in semiconductors, superconductors, medicine, composite materials and so on have been studied [2,3,4,5]. In 2001, fine needle-like crystals composed of C₆₀, "C₆₀ nanowhiskers (C₆₀NWs)" were discovered in a colloidal solution of PZT containing C₆₀ [6]. The liquid-liquid interfacial precipitation method (LLIP method) is a facile technique to synthesize C₆₀NWs, using good solvent solutions of C₆₀ and poor solvents of C₆₀ [7]. Not only the C₆₀NWs but also C₆₀ nanotubes (C₆₀NTs) and C₆₀ nanosheets can be synthesized by the LLIP method by choosing suitable combinations of good solvents and poor solvents of C₆₀ [8,9,10]. The LLIP method have been also applied for the synthesis of C₇₀ nanowhiskers [11], C₇₀ nanotubes [12], the nanowhiskers composed of C₆₀ derivatives like C₆₀[C(COOC₂H₅)₂] and C₆₀ (2-methoxycarbonyl-N-methylpyrrolidine) [13,14], endohedral fullerene nanowhiskers like Sc₃N@C₈₀ nanowhiskers [15] and so forth.

The application study of fullerene nanowhiskers and fullerene nanotubes have been developed recently in field-effect transistors (FETs) [2], solar cells [16] and biosensors like the electrodes using C₆₀NTs deposited with DNA [17].

It has been reported that the factors of light, temperature, growth time, water and the kind and composition of solvents influence the growth of C₆₀NWs when the LLIP method was applied to the synthesis of C₆₀NWs [18,19,20].

Up to now, the growth mechanism of C₆₀NWs has been investigated based on their short-term growth studies. Although a long-term growth observation is necessary to get a thin and long C₆₀NWs, the long-term growth observation has never been

examined until today. Therefore, we have observed the long-term growth process of C₆₀NWs by using optical microscopy and the result is reported here.

2. EXPERIMENTAL

2.1. Synthesis of C₆₀NWs

C₆₀NWs were prepared by use of C₆₀-saturated *m*-xylene solutions and isopropyl alcohol (IPA). In preparing the C₆₀-saturated *m*-xylene solutions, C₆₀ powder (99.5% purity, MTR Ltd., USA) was dissolved in *m*-xylene (98% purity, 0.846g/ml density, as-received non-dehydrated grade, Wako Pure Chemical Industries, Ltd., Japan), ultrasonicated for 30 min and filtered to remove undissolved C₆₀ powder. The C₆₀ saturated *m*-xylene solutions were stored at 5 °C or at 20 °C in incubators (SANYO MIR-153).

In preparing C₆₀NWs by the LLIP method, the C₆₀-saturated *m*-xylene solutions were poured into 10 ml transparent glass bottles and IPA (99.7% purity, 0.786 mg/ml density, as-received non-dehydrated grade, Wako Pure Chemical Industries, Ltd., Japan) was gently added to the C₆₀-saturated *m*-xylene solutions to form liquid - liquid interfaces in a water bath at 5 °C or at 20 °C. The C₆₀NWs were synthesized using the same amount of C₆₀-saturated *m*-xylene solutions and IPA (1:1 in volume ratio). The above glass bottles were stored in incubators at 5 °C or at 20 °C.

2.2. Observations of C₆₀NWs

The observations of C₆₀NWs by optical microscopy were conducted 1-15 days, 20 days, 30 days, 50 days and 100 days after forming the liquid-liquid interfaces, respectively. The C₆₀NWs were sampled from a central part of the precipitates. The lengths of fifty C₆₀NWs were measured for each sample by using an optical microscope (Nikon

ECLIPSE ME600).

Nineteen bottles were prepared for one series of experiments, and each observation was performed using one bottle, and the experiments were repeated three times to get reproducible results.

3. RESULTS AND DISCUSSION

Fig. 1 shows the glass bottle photos of 1 day, 2 days, 3 days, 10 days, 50 days and 100 days after the formation of the liquid-liquid interfaces, respectively. The interfaces between IPA and the C₆₀-saturated *m*-xylene solution can be observed in the bottles of 1 - 3 days. However, the interfaces were lost in the bottles of 5 - 100 days through the mutual diffusion of solvents. The purple color of all the bottles shows the remaining of C₆₀ molecules dissolved in the solutions.

Fig. 1 Photographs of the glass bottles containing C₆₀NWs. The growth periods (days) are shown by the numbers under the bottles. The growth temperature is (a) 5 °C and (b) 20 °C.

Fig. 2 shows optical micrographs and a SEM image of the C₆₀NWs stored at 5 °C. As shown in Figs. 2 (a) and (b), 1 day after the start of growth experiment, a lot of C₆₀NWs with lengths more than 20 μm and granular C₆₀ precipitates were observed as marked by arrows. The average length of C₆₀NWs measured from the optical micrographs is 16.0 ± 7.9 μm, and that measured from the SEM images is 15.4 ± 7.9 μm.

Fig. 2 Optical micrographs of C₆₀NWs prepared by LLIP method and grown at 5 °C for (a) 1 day, (c) 5 days, (d) 10 days, (e) 50 days and (f) 100 days after the start of growth experiment, respectively. (b) SEM image of C₆₀NWs observed 1 day after the start of growth experiment.

In the cases of 5 days (Fig. 2 (c)), 10 days (Fig. 2 (d)) and 50 days (Fig. 2 (e)) after the start of growth experiment, the length of C₆₀NWs was similar to the case of Fig. 2 (a) and no granular C₆₀ precipitates were observed. However, as shown in Fig. 2 (f), 100 days after the start of growth experiment, the long grown C₆₀NWs were observed.

Fig. 3 shows optical micrographs and a SEM image of the C₆₀NWs grown at 20 °C. 1 day after the start of growth experiment (Figs. 3 (a) and (b)), short C₆₀NWs with lengths mostly less than 15 μm were observed. The average length of C₆₀NWs measured from the optical micrographs is 9.7 ± 6.4 μm, and that measured from the SEM images is 8.9 ± 4.8 μm. The measurements by optical microscopy and SEM give the similar length values like the case of Fig. 2.

No granular C₆₀ precipitates were observed in contrast to Fig. 2 (a). However, as shown in the growth periods of 5 days (Fig. 3(c)) and 10 days (Fig. 3(d)), a lot of long C₆₀NWs with lengths mostly greater than 30 μm were observed, accompanying the formation of thick needle-like crystals of C₆₀ shown by arrows.

Fig. 3 Optical micrographs of C₆₀NWs prepared by LLIP method and grown at 20 °C for (a) 1 day, (c) 5 days, (d) 10 days, (e) 50 days and (f) 100 days after the start of growth experiment, respectively. (b) SEM image of C₆₀NWs observed 1 day after the start of growth experiment.

In the growth period of 50 days (Fig. 3 (e)), C₆₀NWs became much longer, and the C₆₀NWs with lengths greater than 50 μm were observed. Further, in the growth period of 100 days, C₆₀NWs with lengths greater than 80 μm were abundantly obtained, including the C₆₀NWs with lengths greater than 100 μm and a lot of thick needle-like crystals. This result may indicate that the formation of thick needle-like crystals can be prevented by the growth at lower temperatures.

Figs. 4 and 5 show the average lengths of C₆₀NWs measured as a function of growth period at 5 °C (Fig. 4) and 20 °C (Fig. 5). The length measurement experiment was performed 3 times at each temperature. In both figures, the average length of C₆₀NWs is shown to oscillate heavily around the fitted curves, which suggests that the growth of C₆₀NWs proceeds by repeating the process of dissolution and reprecipitation.

Fig. 4 Measured average lengths of C_{60} NWs grown at 5 °C as a function of growth period (days) (solid lines). The experiment was repeated three times as shown in (a), (b) and (c). The dotted lines show fitted curves, where the growth period is denoted by x and the length is denoted by y .

Fig. 5 Measured average lengths of C_{60} NWs grown at 20 °C as a function of growth period (days) (solid lines). The experiment was repeated three times as shown in (a), (b) and (c). The dotted lines show fitted curves, where the growth period is denoted by x and the length is denoted by y .

Since the repeated experiments show almost the same growth profiles, it is proved that the experiments were successfully performed with a high reproducibility.

In the early stage of growth, C_{60} NWs were observed to grow faster and longer at 5 °C than at 20 °C. However, this result may have been caused by an artifact of pipetting procedure that would lead to the further growth of C_{60} NWs through the mixing of concentrated *m*-xylene solutions of C_{60} and IPA. The C_{60} NWs grew faster at 20 °C than at 5 °C with increasing the growth period and the longer C_{60} NWs were more abundantly obtained at 20 °C than at 5 °C. Moreover, the average growth rate of C_{60} NWs during the entire experimental period was greater at 20 °C than at 5 °C. Hence, it is found that the long-term growth of C_{60} NWs is enhanced by increasing the growth temperature.

The average growth rate of C_{60} NWs calculated from the fitted curves of Fig. 4 is (a) 0.24 $\mu\text{m}/\text{day}$, (b) 0.20 $\mu\text{m}/\text{day}$ and (c) 0.19 $\mu\text{m}/\text{day}$, respectively, where the average value of these three growth rates is 0.21 $\mu\text{m}/\text{day}$ at 5 °C. Likewise, the average growth rate calculated from Fig. 5 is (a) 0.44 $\mu\text{m}/\text{day}$, (b) 0.47 $\mu\text{m}/\text{day}$ and (c) 0.42 $\mu\text{m}/\text{day}$, respectively, and the averaged growth rate of these three values is 0.45 $\mu\text{m}/\text{day}$ at 20 °C.

Fig. 6 shows the graphs that were obtained by merging all the data of three experiments shown in Figs. 4 and 5. The average growth rate is calculated from the fitted curves as 0.21 $\mu\text{m}/\text{day}$ in Fig. 6 (a) and 0.44 $\mu\text{m}/\text{day}$ in Fig. 6 (b). Hence, it is found

Fig. 6 Graphs of the length of C_{60} NWs as a function of growth period that were obtained by merging the data of three experiments shown in Fig. 4 and Fig. 5. The growth temperature is (a) 5 °C and (b) 20 °C.

that the temperature rise of 15 °C doubly increased the growth rate of C_{60} NWs.

The supersaturation is a very important factor to know the nucleation and growth mechanism in

solution. Although the saturated solubility of C₆₀ in *m*-xylene at 25 °C has been reported to be $4.8 \times 10^{-4} \sim 7.6 \times 10^{-4}$ in mole fraction [21, 22], no solubility data of C₆₀ in *m*-xylene have been reported for the lower temperatures.

Lysozyme forms molecular crystals with Young's moduli of 2.01 - 7.25 GPa [23], and the C₆₀NWs in solution have a similar Young's modulus of 8.9 GPa [24]. The growth rate of a monoclinic lysozyme crystal increases with increasing the supersaturation and reaches 150 μm/h on the (010) face at a supersaturation of about 3.5 at 20 °C [25]. The supersaturation was defined by $\ln(C/C_e)$, where *C* is the lysozyme concentration and *C_e* is an equilibrium concentration. However, the growth rate of C₆₀NWs in our long-term experiment is much smaller than that of the lysozyme crystal by a factor of 10³. The small crystal growth rate of C₆₀NWs is conjectured to be due to a small supersaturation in the C₆₀ - *m*-xylene - IPA system. If the relationship between the supersaturation and the growth rate of lysozyme crystal shown in Figure 2 of ref. [25] is assumed to be applied to the growth of C₆₀NWs, the supersaturation is expected to be close to 1 in the present study. An additional experiment to measure the supersaturation of C₆₀, however, is necessary in order to elucidate the minute growth mechanism of C₆₀NWs in the LLIP method.

4. CONCLUSIONS

The above research can be summarized as follows.

- (1) The C₆₀NWs grown at 5 °C showed an average length greater than that at 20 °C in the initial growth stage of one day. The average lengths of C₆₀NWs were observed to heavily oscillate during the growth period, suggesting that the growth of C₆₀NWs proceeds by repeating the process of dissolution and reprecipitation.
- (2) However, in the long-term (100 days) growth period of C₆₀NWs, the average growth rate of C₆₀NWs was greater at 20 °C than at 5 °C, showing that the long-term growth of C₆₀NWs is enhanced with increasing the growth temperature.
- (3) Thick needle-like crystals of C₆₀ were frequently observed in the glass bottles of 20 °C, suggesting that the growth at the lower temperatures prevents the formation of the thick needle-like crystals.

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