Analysis of the Size of Two-Component C_{60}-C_{70} Fullerene Whiskers

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C_{60}-C_{70} two-component fullerene whiskers were synthesized by a liquid-liquid interfacial precipitation (LLIP) method using various ratios of C_{70} to C_{60}, and were analyzed for their dimensions using scanning electron microscopy (SEM). The diameters and the lengths of the C_{60}-C_{70} fullerene whiskers show ever-increasing W-type graphs which have two local minimal values, respectively. The shape of the graphs were resulted from changing of crystal growth rate with varying of fullerene compositions of mother solution. The carcinogenicity of C_{60}-C_{70} fullerene whiskers can be evaluated using the C_{60}-C_{70} fullerene whiskers whose dimensions and physical factors are specified, and they will be applied to various products such as the active layer materials of solar cells and the anchor materials.

Key words: C_{60}-C_{70} two-component fullerene whisker, Solid solutions, Liquid-liquid interfacial precipitation method, Toxicity, Size analysis

1. INTRODUCTION

Fullerene needle-like crystals with the aspect ratios of 3 or greater and the diameters less than 1000 nm are called fullerene nanowhiskers (FNWs) [1,2]. The FNWs are composed of fullerene molecules such as C_{60}, C_{70}, fullerene derivatives, and endohedral metallofullerenes [1-4].

FNWs can be applied to bulk-hetero-junction type electrode materials and quantum-dot type electrode materials as thin, long and efficient n-type semiconductors or light and flexible superconducting wire rods by alkali-metal doping [5,6]. Fullerene whiskers composed of C_{60} and C_{70} (C_{60}-C_{70} fullerene whiskers) are characterized by the structure analysis and composition analysis using a focused ion beam processing apparatus (FIB-SEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), high-performance liquid chromatography (HPLC), Raman spectroscopy and ultraviolet-visible (UV–vis) spectroscopy, and found to be useful semiconductor materials with the composite effects of high Young’s moduli, large specific strength, small amount of rhombohedral phase, the solid solubility limit of 14 mass% C_{70} or 27 mass% C_{60}, and optical properties of both C_{60} and C_{70} [7,8]. They can be applied to various products such as the active layer materials of solar cells featuring the optical properties of both C_{60} and C_{70} and the anchor materials featuring the large specific strength and the high Young’s moduli.

On the other hand, it is necessary to evaluate the toxicity of FNWs for their application. The toxicity of carbon materials has been evaluated. In human bodies, there are a lot of black spots observed in both lungs due to the inhalation of carbon particles from the air. Several studies suggest that accumulated carbon particles in lungs are proportionally associated with mortality by cancers of lungs or hearts [9-11]. It was reported that the toxicity of multi-walled carbon nanotubes is changed by some factors including diameter, length, rigidity, and surface modification [12]. Furthermore, carcinogenicity of nanofibers are considered to depend on their dimensions and biodegradability according to the theory by Stanton and Pott [13,14]. Hence, it is important to reveal dimensions and biodegradability of FNWs for evaluation of their toxicity. With regard to biodegradability, although untreated FNWs composed of C_{60} (C_{60} NWs) were reported to show high biodegradability and weak cytotoxic effects [15,16], the long C_{60} NWs hardened by a heat treatment under vacuum conditions were reported to exhibit lower biodegradability than that of the untreated C_{60} NWs and abilities to induce the Nod-like receptor pyrin domain containing 3 (Nlrp3)-mediated IL-1b secretion which leads to inflammation [17,18]. With regard to dimensions, we have investigated the diameters and lengths of C_{60} NWs by varying the solution volume, the ratio between good and poor solvents, and the water amount [19,20].

It is necessary to control diameters and lengths of C_{60}-C_{70} fullerene whiskers for evaluation of their carcinogenicity by living-body test using C_{60}-C_{70} fullerene whiskers whose dimensions and physical factors are revealed. In present paper, we investigated the variation of the dimension of the C_{60}-C_{70} fullerene whiskers as a function of the fullerene compositions in the mother solutions in order to consolidate science of size control of the whiskers. They were demonstrated to exhibit the diameters more than 250 nm and the lengths more than 2 µm and can be used as standard samples for evaluation of their carcinogenicity by living-body test and could be applied to various products such as the active layer materials of solar cells and the anchor materials.
2. EXPERIMENTAL

The C_{60}-C_{70} fullerene whiskers were synthesized by a modified liquid-liquid interfacial precipitation (LLIP) method [21]. Fullerene powders (MTR Ltd. C_{60} 99.5%, MTR Ltd. C_{70} 98+%) with various ratios between C_{60} and C_{70} were dissolved in toluene (WAKO JIS special grade) by ultrasonic agitation (Iuchi VS-150). Total fullerene concentration was 2.5 mg to 1 ml of toluene when the fullerene compositions in the mother solutions ranged from 0 to 50 wt% C_{70}. On the other hand, total fullerene concentration was 1.4 mg ml$^{-1}$ when the fullerene compositions in the mother solutions ranged from 70 to 100 wt% C_{70}. The solutions were filtered using syringe filters with 450 nm pores (MITSUBA HIGH GRADE SYRINGE, Whatman 25 mm GD/X) to generate the C_{60}-C_{70} toluene solutions.

4 ml of each mother solution was stored in glass bottles (volume: 10 ml, inner diameter: 18 mm) at 15 °C using a water bath (AS ONE UCT-1000). An equal volume of 2-propanol (WAKO JIS special grade), whose temperature was set to be 15 °C (SANYO MIR-153) in advance, was slowly layered along the inside wall of the bottle onto a mother solution to form a liquid-liquid interface. After forming the interface, the bottle was manually mixed 30 times to achieve homogeneous precipitation, then kept at 15 °C for 2 days to make C_{60}-C_{70} fullerene whiskers grown. Then, the supernatant solution was removed, and 2-propanol was poured into the glass bottle to stabilize the precipitates. After vacuum filtration (KIRIYAMA 5B-21, ULVAC DTC-21), the precipitates were vacuum-dried (AS ONE VO-300) at 100 °C.

The measurements of the size of specimens were performed using a field-emission scanning electron microscope (FE-SEM; Hitachi NB5000). Fullerene composition in the mother solution is determined using high-performance liquid chromatography (HPLC; JASCO UV-2070, PU2089, CO-2065, LC-NetII/ADC).

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the synthesized C_{60}-C_{70} fullerene whiskers with various morphologies. The images show the formation of fine needle-like crystals (nanowhiskers) in (a)-(d), and much larger needle-like crystals in (e)-(j), respectively.

Figures 2 and 3 show the diameters and the lengths of the C_{60}-C_{70} fullerene whiskers as a function of the fullerene composition in the mother solutions (wt% C_{70}), respectively. The C_{60}-C_{70} fullerene whiskers exhibited diameters of 250 nm to 7 µm and lengths of 2 µm to 50 µm. They can be used to living-body test following the theory by Stanton and Pott for evaluating their carcinogenicity.

Here, there are the critical diameters of fullerene whiskers, which are the threshold values and determine the lengths of fullerene whiskers [20]. It was reported that the lengths of fullerene whiskers are a few µm when the diameters of fullerene whiskers are below the critical diameter, and are unlimited and very large when the diameters of fullerene whiskers exceed the critical diameter. Figure 4 shows the relationship among the measured values of diameters of the C_{60}-C_{70} fullerene whiskers, theoretical critical diameters of C_{60} FNWs, and those of C_{70} FNWs. In Figure 4, the measured diameters of the C_{60}-C_{70} fullerene whiskers are less than both the critical diameters of C_{60} FNWs and those of C_{70} FNWs when the fullerene composition in the mother solutions is 5–35 wt% C_{70}, and the measured diameters of the C_{60}-C_{70} fullerene whiskers are more than both the critical diameters of C_{60} FNWs and those of C_{70} FNWs when the fullerene composition in the mother solutions is 45–50 wt% C_{70} or 80–100 wt% C_{70}.

These results from Figure 4 approximately correspond to the measured values of lengths of the C_{60}-C_{70} fullerene whiskers in Figure 3. Thus, the lengths of the C_{60}-C_{70} fullerene whiskers were affected by the diameters of the C_{60}-C_{70} fullerene whiskers.

Figures 2 and 3 show ever-increasing W-type behaviors which have two local minimal values and one local maximal value, respectively. Degree of supersaturation (S) is defined as bellows.

$$S = \frac{C - C_{eq}}{C_{eq}}$$

where C means concentration of fullerenes in the mother solutions and C_{eq} means concentration of fullerenes in the saturated solutions. In this paper, as $S = 14–25$ using C of
The lengths of fullerene whiskers are below the critical diameters of C₆₀ FNWs and those of C₇₀ FNWs. In Figure 4, the measured diameters of the C₆₀-C₇₀ fullerene whiskers as a function of the fullerene composition in the mother solutions (wt% C₇₀). The solutions were filtered using syringe filters with 450 nm pores (MITSUBA HIGH GRADE SYRINGE, JASCO UV-2070, PU2089, CO-2065, LC-NetII/ADC).

In Figure 5, the number density of the C₆₀-C₇₀ fullerene whiskers in the solution as a function of fullerene composition in the mother solutions (wt% C₇₀). The compositions of mother solutions were determined using ultrasonic agitation (Iuchi VS-150). Total fullerene concentration in the mother solutions ranged from 70 to 100 mg ml⁻¹ when the fullerene composition in the mother solutions is 45 wt% C₇₀.

In Figure 6, the theoretical value of crystal growth rate of C₆₀ and C₇₀ as a function of the fullerene composition in the mother solutions (wt% C₇₀). The number density of the C₆₀-C₇₀ fullerene whiskers is determined using microscope (FE-SEM; Hitachi NB5000). Fullerene crystals in (e)-(j), respectively.

In Figure 7, the theoretical value of crystal growth rate of the C₆₀-C₇₀ fullerene whiskers as a function of the fullerene composition in the mother solutions (wt% C₇₀).
1.4–2.5 g l⁻¹ and C₆₀ of 0.1 g l⁻¹, crystal nucleus were stable after nucleation [22]. Hence, crystal size, especially diameters of C₆₀-C₇₀ fullerene whiskers was dependent of number density of C₆₀-C₇₀ fullerene whiskers [23]. The number density of the C₆₀-C₇₀ fullerenes whiskers in the solution is shown in Figure 5. Figure 5 exhibit ever-decreasing M-type behaviors which have two local maximal values and one local minimal value, respectively. The number density of C₆₀-C₇₀ fullerene whiskers was considered to depend on crystal growth rate (R) at the early time of the precipitation, which is defined as followings. [24]

\[
R = a V s \left( C - C_0 \right) \exp \left( -\frac{E_{\text{des}}}{k_B T} \right),
\]

where \(a\) means height of fullerene molecules, \(V_s\) means volume of surfaces of crystals available for precipitation, \(v\) means thermal vibration frequency of fullerene molecules, \(E_{\text{des}}\) means desolvation energy of fullerene molecules, \(k_B\) means Boltzmann constant, and \(T\) means temperature. In this paper, \(a\) is approximately 1 nm, \(v\) is about \(10^{13} \text{s}^{-1}\), \((C - C_0)\) is \(1 - 3 \times 10^{-5} \text{m}^2\) at the early time of the precipitation, \(E_{\text{des}}\) per one molecule is \(1.2 \times 10^{-22} \text{J}\), \(k_B\) is \(1.38 \times 10^{-23} \text{J K}^{-1}\), \(T\) is 288 K, and \(V_s\) at the early time of the precipitation greatly changed from \(10^{15}\) to \(10^{12} \text{m}^3\) with varying of fullerene compositions of mother solution. Using above values, \(R\) of C₆₀ and C₇₀ are calculated to be shown in Figure 6. \(V_s\) of C₇₀ increased at 13.7 wt% C₇₀ which is the solid solubility limit of C₇₀ in the matrix phase of C₆₀ because C₇₀ was able to precipitate at surfaces of most crystals. By the same token, \(V_s\) of C₆₀ increased at 37.4 wt% C₆₀ (26.6 wt% C₆₀) which is the solid solubility limit of C₆₀ in the matrix phase of C₇₀ [8, 24]. Thus, \(R\) of C₆₀ have the maximal value at 13.7 wt% C₆₀ and \(R\) of C₇₀ exhibit the maximal value at 73.4 wt% C₇₀. As theoretical value of \(R\) for the C₆₀-C₇₀ fullerene whiskers is determined by sum of \(R\) of C₆₀ and \(R\) of C₇₀ to be shown in Figure 7, \(R\) of the C₆₀-C₇₀ fullerene whiskers exhibits local maximum at around 13.7 wt% C₆₀ and 73.4 wt% C₇₀. We consider that the behavior of theoretical values of \(R\) corresponds to the behavior of the number density of C₆₀-C₇₀ fullerene whiskers. Therefore, we consider that the diameters of the C₆₀-C₇₀ fullerene whiskers in Figure 2 depend on \(R\) of the C₆₀-C₇₀ fullerene whiskers, and the lengths of the C₆₀-C₇₀ fullerene whiskers were dependent of \(R\) of the C₆₀-C₇₀ fullerene whiskers and the diameters of the C₆₀-C₇₀ fullerene whiskers.

4. CONCLUSION

We have synthesized the C₆₀-C₇₀ fullerene whiskers, which were investigated by the SEM method to conduct the size analysis. They exhibited diameters of 250 nm to 7 µm and lengths of 2 µm to 50 µm and can be used as standard samples to living-body test for evaluating their carcinogenicity or will be applied as the active layer materials of solar cells and the anchor materials. The diameters and the lengths of the C₆₀-C₇₀ fullerene whiskers as a function of the fullerene composition in the mother solutions showed the ever-increasing W-type behavior, which were ascribed to be caused by the nucleation with the crystal growth rate which exhibits local maximum at around 13.7 wt% C₆₀ and 73.4 wt% C₇₀.

References