Synthesis and Structural Analysis of C₆₀-C₇₀ Two-Component Fullerene Nanowhiskers

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Abstract

C₆₀-C₇₀ two-component fullerene nanowhiskers (C₆₀-C₇₀NWs) were synthesized by liquid-liquid interfacial precipitation (LLIP) using various ratios of C₇₀ to C₆₀ and then analyzed using a focused ion beam processing apparatus (FIB-SEM), scanning electron microscopy (SEM), Raman spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD) and high-performance liquid chromatography (HPLC). Both C₆₀ and C₇₀ were saturated in the supernatant solutions with fullerene compositions in the mother solutions ranging from 12.4 mass% C₇₀ to 73.4 mass% C₇₀. C₆₀-C₇₀NWs contained a small amount of rhombohedral phase, indicating polymerization of C₆₀. The solid solubility limit of C₇₀ in the C₆₀ matrix was found to be 13.7 mass%. In addition to fine C₆₀-C₇₀NWs, thick C₆₀-C₇₀ needle-like crystals were formed. The thick C₆₀-C₇₀ needle-like crystals were fractured using a molybdenum probe in the FIB. The fractured surfaces of the C₆₀-C₇₀ needle-like crystals showed modulated structures with chemical compositions characteristic of spinodal decomposition. The activation energy of diffusion was determined to be 37.1 kJ/mol.

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1. Introduction

Fullerenes were first synthesized by Kroto et al. in 1985 [1]. Thereafter, efficient methods of fullerene synthesis, such as the arc discharge method [2] [3], [4] and the combustion method [5] [6], have been developed, and research on fullerenes and fullerene-based materials continue to be conducted throughout the world.

Fullerene molecules bond with each other via van der Waals forces to form molecular crystals. In particular, fullerene needle-like crystals with aspect ratios of 3 or greater and diameters less than 1000 nm are called fullerene nanowhiskers (FNWs) **Error! Reference source not found.** [8]. FNWs were first observed in a colloidal solution of PZT containing C₆₀ in 2001 [9] [10]. In 2002, a liquid-liquid interfacial precipitation method was developed to efficiently synthesize FNWs [11].

FNWs are recyclable, as fullerene molecules can be recovered by redissolving the FNWs into organic solvents such as toluene and benzene. FNWs exhibit semiconductor properties and can potentially be used for field-effect transistors [12], solar cells [13], fuel cells [14] [15], catalysts [8] [16], [17], [18], [19], [20], biosensors [21] and chemical synthesis templates [8].

To date, studies of **C₆₀ nanowhiskers (C₆₀NWs)** have been reported. Because the electrical resistivity of C₆₀NWs is approximately proportional to diameter to the third power **Error! Reference source not found.**, the electrical properties of C₆₀NWs vary from insulator to semiconductor depending on diameter. In addition, C₆₀NWs become conductive glass-like carbon nanofibers following high-temperature heat treatment in an inert atmosphere [22]. Additionally, C₆₀NWs can be made into superconductors by doping with alkali metals such as potassium [23] [24]. The Young's moduli of C₆₀NWs

are 32 to 54 GPa [25], approximately 30 to 60 percent of the moduli of single-crystal silicon.

Numerous types of FNWs with various new physical properties can be synthesized by combining different fullerene molecules. Synthesis of C_{60} - C_{70} nanowhiskers (C_{60} - C_{70} NWs) was reported in 2004 [26]. The Young's moduli of C_{60} - C_{70} NWs were measured by a transmission electron microscope equipped with atomic force microscope functionality and were found to increase with increasing C_{70} content in the mother solutions [27]. This increase in Young's modulus is assumed to be caused by the formation of a C_{60} - C_{70} solid solution that induces hardening, i.e., solid solution hardening. C_{60} - C_{70} NWs have absorption bands of both C_{60} and C_{70} . C_{60} - C_{70} NWs hold potential for semiconductor devices as a new composite material with high Young's moduli and optical properties of both C_{60} and C_{70} .

However, despite the various promising properties of C_{60} - C_{70} NWs, the structural, chemical and optical properties of C_{60} - C_{70} NWs are not well understood. The objective of the present paper is to investigate the structural, chemical and optical properties of these FNWs 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.

2. Experimental

Powders of C_{60} (MTR Ltd., 99.5%) and C_{70} (MTR Ltd., 99.0%) were dissolved in toluene (WAKO JIS special grade) by ultrasonic agitation (Iuchi VS-150). The solutions were filtered using syringe filters (MITSUBA HIGH GRADE SYRINGE, Whatman 25 mm GD/X) to generate a C_{60} -saturated toluene solution and a C_{70} -saturated toluene solution.

The C₆₀-saturated and C₇₀-saturated toluene solutions were mixed in various ratios to form C₆₀-C₇₀ two-component mother solutions. The mixing ratios were (10.0 mL [C₆₀], 0 mL [C₇₀]), (9.5, 0.5), (9.0, 1.0), (8.5, 1.5), (8.0, 2.0), (7.0, 3.0), (6.0, 4.0), (5.0, 5.0), (4.0, 6.0), (3.0, 7.0), (2.0, 8.0), (1.5, 8.5), (1.0, 9.0), (0.8, 9.2), (0.6, 9.4), (0.5, 9.5), (0.4, 9.6), (0.2, 9.8) and (0, 10.0).

The temperature of each mother solution, stored in glass bottles (volume: 30 ml, inner diameter: 27 mm), was set to 15 °C using a water bath (AS ONE UCT-1000). 10 ml of 2-propanol (WAKO JIS special grade) was slowly layered along the inside wall of the bottle onto an equal volume of fullerene-saturated toluene solution to form a liquid-liquid interface. After forming the interface, the bottle was manually mixed 30 times, then kept still at 15 °C (SANYO MIR-153) for 5 days to complete fullerene precipitation. Then, the supernatant 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 room temperature.

Structural analysis of specimens was performed by XRD (Rigaku Ultima III) and a FIB-SEM (Hitachi NB5000) equipped with a Ga ion beam source and a field-emission scanning electron microscope (FE-SEM).

Chemical compositions of the specimens was analyzed by HPLC (JASCO UV-2070, PU 2089, CO-2065, LC-Net II /ADC) and Raman spectrometry (JASCO NRS-3000).

The optical properties of the specimens were investigated by ultraviolet-visible spectroscopy (UV-Vis, JASCO V-570). The measurement was performed for the vacuum-dried powder of FNWs by the diffuse reflection method using an integrating sphere.

3. Results and Discussion

The mother solutions were analyzed by HPLC, the chemical composition of each mother solution was determined.

Figure 1 shows optical microscope images of the synthesized precipitates with various morphologies and metallic lusters. The images show the formation of fine needle-like crystals (nanowhiskers) in (a), (b) and (f), much bigger needle-like crystals in (c) and (d) and fine granular precipitates in (e).

Figure 2 shows X-ray diffraction patterns of synthesized C_{60} NWs (a) and of C_{60} - C_{70} NWs synthesized using a mother solution with a composition of C_{60} - 24 mass% C_{70} (b). Peaks corresponding to a face-centered cubic (fcc) phase and a triclinic (tr) phase can be assigned in the C_{60} NWs. It is likely that the tr phase was formed by distortion of the fcc phase [28]. The lattice constant of the fcc phase was determined to be $a = 1.422 \pm 0.005$ nm. Peaks corresponding to a rhombohedral phase (rh) in addition to the fcc phase and the tr phase were also observed in the C_{60} - C_{70} NWs. It has been reported that C_{60} can be transformed to a polymer with an rh phase by high-temperature high-pressure treatment [29]. It is likely that partial polymerization of C_{60} molecules was caused by the addition of C_{70} molecules. The lattice constant of the fcc phase was determined to be $a = 1.433 \pm 0.011$ nm, 0.77% larger than the C_{60} NW lattice constant ($a = 1.422 \pm 0.005$ nm). Table 1 shows the lattice constants and primitive unit cell volumes of C_{60} NWs and C_{60} - C_{70} NWs.

Figure 3 shows the UV-Vis absorption spectra of C_{60} NWs and C_{60} - C_{70} NWs synthesized using a mother solution with a composition of C_{60} - 24 mass% C_{70} . The hyperchromic effect and a bathochromic shift were observed for the C_{60} - C_{70} NWs compared to the C_{60} NWs. The C_{60} - C_{70} NWs have a wider light absorption band than the C_{60} NWs, showing stronger absorption especially around 600 nm. This is caused by the wider and stronger absorption range of C_{70} than C_{60} [30].

The composition of C_{60} - C_{70} two-component specimens was measured by Raman spectroscopy and calculated using the peak area ratios, $100 \times S_2 / (S_1 + S_2)$, where S_i is

the peak area of Ag(2) and S₂ is the peak area of A₁'(6) [31]. A linear relationship was assumed to hold between the peak area ratio and the fullerene composition (mass% C₇₀).

Figure 4 shows the chemical composition of the C₆₀-C₇₀NW surfaces and the granular precipitates as determined by Raman spectroscopy. When the composition of fullerene in the mother solution is 9 mass% C₇₀, the granular precipitates and the C₆₀-C₇₀NWs have similar compositions. However, when the composition of fullerene in the mother solution is at least 18 mass% C₇₀, the composition of fullerene (mass% C₇₀) in the granular crystals is much higher than in the C₆₀-C₇₀NWs. It is likely that the granular precipitates are rich in C₇₀ precipitate when the fullerene composition (mass% C₇₀) in the mother solutions exceeds the solid solubility limit of C₇₀ in the C₆₀ matrix phase.

Chemical composition analysis for the supernatant solutions was performed as shown in Figure 5. This figure can be divided into three regions (I, II, III). The boundary between I and II is located at 12.4 mass% C₇₀, and the boundary between II and III is located at 73.4 mass% C₇₀. Figure 5 indicates that the solid solubility of C₇₀ in the matrix phase of C₆₀ is 12.4 mass% and that the solid solubility of C₆₀ in the matrix phase of C₇₀ is 26.6 mass%. The chemical compositions of the precipitates determined by HPLC are shown in Figure 6. Figure 5 shows that C₇₀ is unsaturated in the supernatant solutions for compositions ranging from 0 mass% C₇₀ to 12.4 mass% C₇₀, corresponding to region I of Figure 6. Figure 5 also shows that C₆₀ is unsaturated in the supernatant solutions for compositions ranging from 73.4 mass% C₇₀ to 100 mass% C₇₀, corresponding to region III of Figure 6. Both C₆₀ and C₇₀ are saturated in the supernatant solutions for compositions ranging from 12.4 mass% C₇₀ to 73.4 mass% C₇₀, corresponding to region II of Figure 6.

Table 2 shows the chemical compositions of the thick C₆₀-C₇₀ needle-like crystals determined by HPLC. HPLC analyses of the thick needle-like crystals were performed on individual crystals selected using fine probes. Thick C₆₀-C₇₀ needle-like crystals

contain 11.1 ± 2.2 mass% C_{70} , up to 13.7 mass% C_{70} . It was found that the solid solubility of C_{70} in the matrix phase of C_{60} is 13.7 mass%. This result corresponds with the result from Figure 5 (12.4 mass%) as well as previous reports [32] [33].

Figure 7 shows SEM images of a fracture process for a thick C_{60} - C_{70} needle-like crystal synthesized using the mother solution with a composition of C_{60} - 45 mass% C_{70} . Image (a) shows a notch formed by sputtering with Ga ion beams and a fixed part by deposition of tungsten (W). In images (b), (c) and (d), the C_{60} - C_{70} needle-like crystal was slowly bent by a molybdenum probe and fractured.

Figure 8 shows SEM images of the fracture surfaces of the C_{60} - C_{70} needle-like crystals. The areas surrounded by the red lines are the areas measured for chemical composition by Raman spectroscopy. Figure 9 shows the fullerene composition of the fractured surfaces. The fractured surfaces exhibited sinusoidally modulated compositions.

Spinodal decomposition is a phenomenon involving spontaneous biphasic separation, with a sinusoidally modulated structure occurring after a finite time. We believe that these modulated structures result from spinodal decomposition. In Figure 9, the wavelength of spinodal decomposition is 7.44 ± 2.45 μm . The diffusion length must be comparable to half of the wavelength of spinodal decomposition (3.72 μm). The diffusion length was calculated based on the following equation [34], [35], [36].

$$L = \sqrt{D \cdot t}, \quad D = \frac{1}{6} \cdot \lambda^2 \cdot \beta \cdot \nu_0 \cdot \exp\left(-\frac{Q}{RT}\right), \quad \beta = \exp\left(\frac{S}{k_B}\right)$$

L is the average diffusion length. t is diffusion time, which is 5 days in the present paper. D is the diffusion coefficient. λ is the particle migration length, which is calculated to be $1.433 / \sqrt{2} = 1.013$ nm using the lattice constant from Table 1. β is the number of microscopic states and ν_0 is the particle vibration frequency. R is the gas constant. S is the entropy and k_B is Boltzmann constant. Q is the activation energy of diffusion, which is equivalent to the binding energy between particles. $L = 0.008596 \times \exp(-Q / 4789)$

[m], assuming $\beta = 1$ and $\nu_0 = 10^9 \text{ s}^{-1}$ for $T = 15 \text{ }^\circ\text{C}$. When L equals $3.72 \text{ }\mu\text{m}$, Q is calculated to be 37.1 kJ/mol from Figure 10.

4. Conclusions

- (1) The $\text{C}_{60}\text{-C}_{70}\text{NWs}$ contained a small amount of rhombohedral phase and showed an fcc lattice constant that is 0.77% larger than that of C_{60}NWs .
- (2) The $\text{C}_{60}\text{-C}_{70}\text{NWs}$ showed a stronger visible light absorption than C_{60}NWs , especially at 600 nm.
- (3) Both C_{60} and C_{70} are saturated in the supernatant solutions when the composition of fullerene in the mother solutions ranges from 12.4 mass% C_{70} to 73.4 mass% C_{70} .
- (4) The solid solubility limit of C_{70} in the matrix phase of C_{60} is 13.7 mass%.
- (5) C_{70} molecules precipitate as granular crystals when the concentration of C_{70} in the mother solutions exceeds the solid solubility limit of C_{70} in C_{60} .
- (6) The fractured surfaces of $\text{C}_{60}\text{-C}_{70}$ needle-like crystals showed modulated structures and chemical compositions, indicating spinodal decomposition. The activation energy of diffusion was calculated to be 37.1 kJ/mol .

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Figure captions

Table 1. Lattice constants of C₆₀NWs and C₆₀-C₇₀NWs.

Table 2. Chemical composition of the thick C₆₀-C₇₀ needle-like crystals determined by HPLC.

Fig. 1. Optical images of the precipitates. The compositions of mother solutions were (a) C₆₀- 9 mass% C₇₀, (b) C₆₀- 24 mass% C₇₀, (c) C₆₀- 37 mass% C₇₀, (d) C₆₀- 45 mass% C₇₀, (e) C₆₀- 78 mass% C₇₀, (f) 100 mass% C₇₀.

Fig. 2. XRD patterns of (a) the C₆₀NWs and (b) the C₆₀-C₇₀NWs obtained using a mother solution with a composition of C₆₀- 24 mass% C₇₀.

Fig. 3. UV-Vis spectra of the C₆₀NWs and the C₆₀-C₇₀NWs obtained using a mother solution with a composition of C₆₀- 24 mass% C₇₀.

Fig. 4. Chemical composition of the granular crystals and the C₆₀-C₇₀NWs determined by Raman spectroscopy.

Fig. 5. Chemical composition of the supernatant solutions determined by HPLC.

Fig. 6. Chemical composition of the precipitates determined by HPLC.

Fig. 7. SEM images of the fracture process of a C₆₀-C₇₀ two-component needle-like crystal.

Fig. 8. SEM images of the fractured cross-sections of C₆₀-C₇₀ two-component needle-like crystals. The areas surrounded by red lines were measured by Raman spectroscopy.

Fig. 9. Chemical composition of the fractured cross-sections of C₆₀-C₇₀ needle-like crystals. (a), (b), (c), (d) and (e) in Fig. 9 correspond to (a), (b), (c), (d) and (e) in Fig. 8, respectively. The red arrows and circles in Fig. 9 correspond to those in Fig. 8.

Fig. 10. Relationship between the diffusion length and the activation energy of C₆₀ molecules calculated using $t = 5$ days, $\lambda = 1.013$ nm, $\beta = 1$, $\nu_0 = 10^9$ s⁻¹ and $T = 15$ °C.

Table 1. Lattice constants of C₆₀NWs and C₆₀-C₇₀NWs.

Specimens	Crystal system	Lattice constant (nm)	Primitive unit cell volume (nm ³)
C ₆₀ NWs	Face-centered cubic (fcc)	$a=1.422 \pm 0.005$	0.719
	Triclinic (tr)	$a=0.950, b=1.000$ $c=1.010, \alpha=74.9^\circ$ $\beta=59.4^\circ, \gamma=60.0^\circ$	0.715
C ₆₀ -C ₇₀ NWs	fcc	$a=1.433 \pm 0.011$	0.736
	tr	$a=0.951, b=0.954$ $c=1.018, \alpha=75.4^\circ$ $\beta=60.0^\circ, \gamma=60.0^\circ$	0.693
	Rhombohedral (rh)	$a=1.174, c=1.652$	0.657

Table 2. Chemical composition of the thick C₆₀-C₇₀ needle-like crystals analyzed by HPLC.

	Mother solution	Thick C ₆₀ -C ₇₀ needle-like crystals	
		Average	Maximum
Composition of fullerene (mass% C ₇₀)	45.4 ± 4.1	11.1 ± 2.2	13.7

Fig. 1.

Fig.2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.