GC-MS analysis of the solvents contained in C\textsubscript{60} nanowhiskers

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Abstract. The solvent molecules contained in C\textsubscript{60}NWs affect not only the shape but also the crystal structure of C\textsubscript{60}NWs. The solvents contained in C\textsubscript{60}NWs were found to be toluene and IPA by the GC-MS analysis. The most abundant solvent was toluene and the quantity of residual toluene in the as-prepared C\textsubscript{60}NWs was about 7 mass\%. The quantity of impurity solvents is reported for the as-prepared, air-dried, vacuum-dried and heat-treated C\textsubscript{60}NWs.

1. Introduction
Solution-grown C\textsubscript{60} crystals have various structures and shapes that depend on organic solvent, growth temperature and so on. Recently, a new type of C\textsubscript{60} needle-like crystals called C\textsubscript{60} nanowhiskers (C\textsubscript{60}NWs) were obtained in a solution by the liquid-liquid interfacial precipitation (LLIP) method, where the C\textsubscript{60} nanowhiskers nucleate at the interface between a toluene solution of C\textsubscript{60} and isopropyl alcohol [1]. Typical C\textsubscript{60}NWs have diameters less than 500 nm and lengths greater than a few micrometers. The high aspect ratio of C\textsubscript{60}NWs with the small diameter is very unique, compared with those of any needle-like C\textsubscript{60} crystals reported previously.

Same as C\textsubscript{60} crystals, the shape of C\textsubscript{60}NWs varies depending on the growth solution and growth condition [2-5]. For example, fullerene nanotubes, nanoporous fullerene nanowhiskers and fullerene nanosheets are synthesized by use of pyridine, benzene and CCl\textsubscript{4}, respectively. The C\textsubscript{60}NWs in solution have a hexagonal solvated structure and their growth direction is parallel to the [0001] direction. The hexagonal solvated structure rapidly changes into the face-centered cubic (fcc) structure by drying through the evaporation of solvent molecules in air or in vacuum [6]. The solvent molecules included in C\textsubscript{60}NWs affect not only the shape but also crystal structure. However, there are really few studies about the solvents contained in C\textsubscript{60}NWs [7, 8]. In this report, the solvent molecules contained in C\textsubscript{60}NWs are examined by use of GC–mass spectrometry (GC-MS) for the as-prepared specimens, the specimens dried in vacuum and the heat-treated specimens.

2. Experimental

2.1. Samples
C\textsubscript{60}NWs were grown by the LLIP method as reported previously [1]. A toluene (99.5\% Wako Ltd.) solution saturated with C\textsubscript{60} (99.95 \% MTR Ltd.) was prepared and poured into a glass bottle. Next,
isopropyl alcohol (IPA, 99.8% Wako Ltd.) was gently added to the solution to form a liquid-liquid interface. After the addition of IPA, the solution was manually mixed for a few times and was kept in an incubator (SANYO MIR-153) at 20 °C for 24 h.

2.2. Drying and heat treatment of samples
The C_{60}NWs grown in solutions were dispersed in IPA and collected by the centrifugal method. The C_{60}NWs were treated by three methods before the measurement by GC-MS. The first method is air drying, the second method is vacuum drying in a vacuum furnace and the third method is the heat treatment in Ar gas. The samples were dried in vacuum of a range of 10^{-2} and 10^{-4} Pa for 5 ~ 720 min. In the heat treatment in Ar, the air in the vacuum furnace was substituted by pure Ar (99.999%), and the C_{60}NWs were heated at 50 °C to 300 °C for 30 min. The C_{60}NWs were put in disposable containers (Eco-cap, Frontier Laboratories Ltd.) and heat-treated in Ar.

2.3. Measurement conditions by GC-MS
A thermal desorption (TD) method was used to measure the solvents contained in C_{60}NWs. Since C_{60} sublimates at about 300 °C in vacuum [9], the heating temperature was set at 350 °C. It was expected that the solvent molecules contained in the matrix of C_{60}NWs were instantaneously detached at 350 °C, where the TD system with Double-Shot Pyrolyzer (Frontier Laboratories Ltd. PY-2020iD) was used. The gases from C_{60}NWs were analyzed by GC-MS system (SHIMADZU GCMS-2010) using a split rate of 1:100. The gas chromatography (GC) was performed at an injection temperature of 330 °C, using a helium carrier gas pressure and a column composed of 5% diphenyl and 95% dimethylpolysiloxane (Ultra ALLOY+, Frontier Laboratories Ltd.). The oven was heated from 40 °C to 300 °C at a heating rate of 30 °C min^{-1}. The mass analysis was done by using the EI+ ionization mode at an interface temperature of 330 °C.

![Figure 1. The calibration curve for the quantitative analysis of toluene. The horizontal axis expresses the concentration of toluene (mass ppm). The vertical axis expresses the peak area ratio of toluene versus tetracene standard.](image)

About 300 ~ 550 μg of C_{60}NWs were collected by centrifugation and used in each measurement by GC-MS. Before the GC-MS analysis, the sample cases containing the C_{60}NWs other than air drying were dried in vacuum for 5 min at room temperature in order to remove the solvents adsorbed on the surface of C_{60}NWs. Tetracene was used as a standard material. 0.0025 g of tetracene was dissolved in 50 ml of hexane. 100 μL of tetracene-hexane solution was put into a sample case and heated at 50 °C on a heater in order to evaporate only hexane and about 5 μg of tetracene remained in the sample case. The C_{60}NWs dried in vacuum for 5 min were put into the same sample case containing 5 μg tetracene and subjected to the GC-MS analysis. The other samples were also similarly treated and subjected to the GC-MS analysis. A calibration curve for the quantitative analysis of toluene was made to measure the amount of residual toluene contained in C_{60}NWs as shown in Figure 1. The horizontal axis expresses the concentration of toluene (mass ppm). The vertical axis expresses the peak area ratio of
toluene versus the tetracene standard. 1, 2, 5 and 10 mg of toluene were diluted with 10 ml of hexane. The calibration curve was made by using 2 μL of the hexane solutions of toluene with the concentrations of 1, 2, 5 and 10 μg μL⁻¹, and 5 μg of tetracene for GC-MS at the same time. The amount of residual toluene contained in C₆₀NWs was measured with the calibration curve.

3. Results and discussion

Figure 2 shows a GC-MS analysis of C₆₀NWs after drying in vacuum for 5 minutes. In figure 2(a), there are four peaks labeled at 0.925, 1.067, 2.33 and 10.09 min. In Figure 2(a), the peak of 0.925 min is consistent with the ions originated from CO₂, N₂ and water. Hence, the surface of C₆₀NWs must have adsorbed water, CO₂ and N₂. But the peak may contain the air introduced into the GC-MS system at the time of sample injection. All of the measured CO₂, N₂ and water may not have been from the surface of C₆₀NWs. Figure 2(b) shows the mass spectra for the peak labeled at 2.33 min with the major ions at 91 and 92 Da. The molecular weight of toluene is 92, and the peak of 91 Da shows the fragments formed by the elimination of hydrogen atoms from toluene molecules in the electron ionization chamber. Figure 2(c) shows the mass spectra for the peak labeled at 1.067 min with the major ions at 45, 59 and 43 Da. The peak of 45 Da shows the fragments of isopropyl alcohol molecules formed by the elimination of –CH₃ groups and the peak of 43 Da shows the fragments formed by the elimination of –OH groups. The peak labeled at 10.09 min is due to the tetracene standard. The amount of residual toluene is more abundant than IPA. This is consistent with the fact that C₆₀ is hardly dissolved in polar solvents like alcohol. Next, the most abundant toluene contained in the matrix of C₆₀NWs is quantitatively analyzed by use of the peak area ratio of toluene versus tetracene.

![Figure 2](image)

Figure 2. GC-MS analyses of C₆₀NWs. (a) GC spectrum of C₆₀NWs after drying in vacuum for 5 min, (b) the mass spectra corresponding to the peak of 2.33 min in (a) and (c) the mass spectra corresponding to the peak of 1.067 min in (a).

The amount of residual toluene contained in the vacuum-dried C₆₀NWs is roughly in proportion to the sample weight of C₆₀NWs. Figure 3 shows the amount of toluene measured by using the analytical curve of Figure 1 as a function of the weight of C₆₀NWs. Figure 3 shows that the amount of residual toluene in each sample of C₆₀NWs increases linearly with increasing the weight of C₆₀NWs.
Sample weight of C60NWs (μg)

Figure 3. The amount of residual toluene contained in the C60NWs measured by use of the calibration curve of Figure 1 as a function of the sample weight of C60NWs dried in vacuum for 5 min at room temperature.

Next, the change of the toluene content in the C60NWs (mass %) subjected to the air drying and that of the C60NWs dried in vacuum at room temperature are shown in Figure 4. The C60NWs were dried for 30, 60, 120 and 240 min in air, respectively. The toluene content for the as-prepared C60NWs is also shown. The content of residual toluene in the C60NWs shows similar values for the drying time of 30 to 240 min. The as-prepared C60NWs show about 7 mass % of toluene content. It has been reported that hexagonal solvated structures of C60NWs rapidly change into fcc structures upon drying through the evaporation of solvent molecules [6], corresponding to the present decrease of toluene in the C60NWs. Figure 4 also shows the data of C60NWs dried in vacuum at room temperature for 5, 120 and 720 min, respectively. The quantity of residual toluene decreased to about 1 % from 3.2 % in the C60NWs that were dried in vacuum at room temperature for 120 min. But the residual toluene was not completely removed even for the elongated vacuum drying of 720 min. Hence, part of the toluene molecules contained in the matrix of C60NWs must be tightly trapped by some special sites of C60 crystal lattices.

Figure 4. Change of the content of residual toluene in the dried C60NWs as a function of drying time. Filled rectangles (■) show the residual toluene contained in the C60NWs after air drying at room temperature for 30, 60, 120 and 240 min, respectively, and that of the as-prepared C60NWs. Filled diamonds (◆) show the residual toluene contained in the C60NWs dried in vacuum at room temperature for 5, 120 and 720 min.

Figure 5 shows the residual toluene content of the C60NWs heated at 50, 100, 200 and 300 °C for 30 min in Ar gas and that of the C60NWs dried in vacuum for 5 min at room temperature. The toluene content in the C60NWs decreased to about 0.2 % from the initial content of 3.2 % rapidly by the heat treatment at 100 °C. Since the C60NWs heat-treated at high temperatures turn to porous structures [12],...
the contained solvent molecules are expected to escape easily through the formed pores. However, the residual toluene content shows the similar values in the C$_{60}$NWs heat-treated at 100, 200 and 300 °C. This result also suggests that part of the contained toluene molecules are tightly bound to some special sites of C$_{60}$ lattices and cannot be easily removed by the heat treatment.

![Figure 5](image)

**Figure 5.** Change of the residual toluene content in the heat-treated or vacuum-dried C$_{60}$NWs expressed as a function of heating temperature. The C$_{60}$NWs were heated in Ar gas at each temperature for 30 min.

![Figure 6](image)

**Figure 6.** Raman shifts of $A_g(2)$ mode in the as-prepared C$_{60}$NWs, the C$_{60}$NWs dried in vacuum for 5 min at room temperature and the C$_{60}$NWs heated in Ar gas at 100 - 300 °C for 30 min.

The small amount of residual toluene molecules may alter the mechanical and electrical properties of C$_{60}$NWs from those of pure C$_{60}$ crystals. In the Raman spectroscopy of C$_{60}$, it is known that the position of $A_g(2)$ peak is very sensitive to the polymerization of C$_{60}$ [10, 11]. In the C$_{60}$ nanotubes prepared by use of a C$_{60}$-saturated pyridine solution and IPA, a remarkable difference in the peak position of $A_g(2)$ mode was observed between the as-prepared solvated C$_{60}$ nanotubes and the C$_{60}$ nanotubes heat-treated at 100 to 500 °C [12]. The position of $A_g(2)$ peak was also measured in the present experiment for the as-prepared and heat-treated C$_{60}$NWs as shown in Figure 6. The average value of the Raman shifts of the C$_{60}$NWs heat-treated at 100 to 300 °C and that of the C$_{60}$NWs dried in vacuum at room temperature is 1466.2 ± 0.25 cm$^{-1}$, while the as-prepared solvated C$_{60}$NWs show the Raman shift of 1464.1 ± 1.7 cm$^{-1}$. From the above results of GC-MS spectrometry, it is found that the difference in the Raman shift between the as-prepared C$_{60}$NWs and the heat-treated C$_{60}$NWs is caused by the difference in the amount of solvent molecules contained in the C$_{60}$NWs. The weak peak shift of $A_g(2)$ mode in the as-prepared C$_{60}$NWs from 1469 cm$^{-1}$ of pristine C$_{60}$ [11] must be owing to a slight...
distortion of C_{60} molecules from their spherical icosahedral symmetry that is caused by the interaction between the C_{60} molecules and the surrounding solvent molecules.

4. Conclusions
The present research can be summarized as follows.

(1) Toluene was most abundantly contained in the C_{60}NWs.
(2) The content of toluene was 7% in the as-prepared C_{60}NWs and rapidly decreased upon the heat treatment in vacuum or drying in the air.
(3) The down shift of A_{4}(2) peak observed in the as-prepared solvated C_{60}NWs is assumed to be caused by the weak interaction between C_{60} molecules and the residual toluene molecules that deforms the spherical icosahedral symmetry of C_{60}.

In order to understand the mechanism of structural stability of solvated C_{60}NWs, it is necessary to study the time evolution between the amount of residual IPA and toluene contained in the C_{60}NWs and the crystal structural change of the C_{60}NWs upon drying. We are going to investigate this theme further.

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