Formation and structures of C$_{60}$ nanowhiskers with high strength and large elasticity

Mami Watanabe$^1$, Takahiro Yamamoto$^1$, Kenichi Kojima$^1$, Makoto Tanimura$^2$ and Masaru Tachibana$^1$*

$^1$International Graduate School of Arts and Sciences, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236-0027, Japan
$^2$Research Department, NISSAN ARC, LTD., Natsushima-cho, Yokosuka 237-0061, Japan

E-mail address: tachiban@yokohama-cu.ac.jp

Abstract. Formation and structure of toughened C$_{60}$ nanowhiskers (C$_{60}$NWs) were investigated. C$_{60}$NWs are modified when pristine ones grown by a liquid-liquid interfacial precipitation method are kept in the growth solution for more than 3 years. The modified ones have a hexagonal solvated structure not only in the solution but also in air or a vacuum. The modified ones exhibit high strength and large elastic deformation in air, quite differing from the brittle in pristine ones in air.

1. Introduction

A new type of C$_{60}$ needle-like single crystals called C$_{60}$ nanowhiskers (C$_{60}$NWs) has been grown by a liquid-liquid interfacial precipitation (LLIP) method, where they nucleate at the interface between a toluene solution of C$_{60}$ and isopropyl alcohol [1]. Typical C$_{60}$NWs have less than 500 nm in diameter and more than 100 $\mu$m in length. Especially, C$_{60}$NWs exceeding 1 mm in length can be easily obtained [2]. Such unique shapes of C$_{60}$NWs can provide us with various applications such as nano-scale electronic devices and field emitters. Some mechanical [3] and electrical properties [4] of C$_{60}$NWs have been already reported.

Pristine C$_{60}$NWs in the growth solution have a hexagonal solvated structure and their growth direction corresponds to a [0001] direction [5]. C$_{60}$ molecules in the nanowhiskers are condensed with van der Waals force [2]. The hexagonal solvated structure is easily changed by drying, i.e. the evaporation of solvent molecules in air or a vacuum [5]. Consequently, the dried C$_{60}$NWs have a face-centered cubic (fcc) structure where the long axis corresponds to a [110] direction. The perfection in dried C$_{60}$NWs is low compared with pristine ones [6]. In addition, the dried ones are brittle and relatively soft. The mechanical weakness in C$_{60}$NWs in air or a vacuum is a severe problem for the practical applications. On the other hand, it seems that pristine C$_{60}$NWs in the growth solution have large elastic deformation and are relatively tough [6]. For the practical applications, it is desired that such mechanical toughness in pristine C$_{60}$NWs are kept even in air or a vacuum.

Recently we found that C$_{60}$NWs kept in the growth solution for more than 3 years show higher strength and larger elastic deformation in air. The production of such toughened C$_{60}$NWs might lead to...
a breakthrough for the practical applications. In this paper, we report the formation and structure of toughened C$_{60}$NWs.

2. Experimental procedure

C$_{60}$NWs were grown by the LLIP method as reported previously [7]. C$_{60}$NWs grown for more than one month exceed 1 mm in length but are still below 500 nm in diameter. C$_{60}$NWs grown for about 1 week to several months were defined as “pristine” specimens. Moreover, C$_{60}$NWs kept in the growth solution for more than 3 years was called as “3-years” ones. These two kinds of specimens were investigated in this work. The LLIP method included some C$_{60}$ bulk crystals as impurities. They predominantly contribute to X-ray diffraction (XRD) and Raman spectra. To obtain intrinsic XRD and Raman spectra of C$_{60}$NWs, specimens were purified by several filtrations. The purified ones were used in the measurements.

The surface of C$_{60}$NWs was observed by scanning electron microscopy (SEM) (S-4700, Hitachi). The structure and intermolecular interaction of C$_{60}$NWs were examined by XRD (RINT X-ray Diffractometer, Rigaku) and Raman spectroscopy (FRA 106/S, Bruker). To clarify their features in the growth solution and air, time evolution of the XRD and Raman spectra of C$_{60}$NWs during the drying was measured. In the XRD measurements, the specimens were mounted on a glass sample holder immediately after the sampling from the growth solution. XRD patterns were taken with a 0.1542 nm of Cu K$_\alpha$. In the Raman measurements, the specimens were mounted on a mirror immediately after the sampling from the growth solution. The Raman spectra were taken with a 1064 nm excitation from a YAG laser in order to avoid the photo-polymerization of C$_{60}$ by the excitation.

The mechanical properties of 3-years ones in air were investigated by a bending method. To observe the bending behavior, the specimens were mounted on the glass plate with droplets, from the growth solution. The bending deformation for specimens was carried out by applying a wind pressure with a fan as reported previously [6]. In order to apply larger stress, the tip of specimen was manually

![Figure 1](image)

**Figure 1.** SEM images of (a) pristine C$_{60}$NWs, and (b) 3-years ones that were formed when pristine ones were kept in the growth solution for more than 3 years. (c) and (d) show expanded figures for (a) and (b), respectively.
pushed by using a needle. However, the stress applied to the specimen could not be measured in this experiment. The observation of the bending behavior was carried out in-situ by using an optical microscope (BX51, Olympus) with a charge coupled device (CCD).

3. Results and discussion

Figure 1(a) and 1(b) show SEM images of pristine C\textsubscript{60}NWs, and 3-years ones that were formed when pristine ones were kept in the growth solution for more than three years, respectively. As shown in figure 1(a) and 1(b), straight and curved C\textsubscript{60}NWs are clearly observed for both specimens. Some bundles are also observed. In addition, as seen in the expanded figures of figure 1(c) and 1(d), the shape of cross section of each C\textsubscript{60}NW is found to be hexagonal-like one for both specimens. However, the surface in 3-years ones in figure 1(d) is much rough compared with that in pristine ones in figure 1(c). According to the preliminary gas chromatograph mass spectrometric analysis, oxides originated from toluene and some other products were observed only for 3-years ones. Therefore, the surface roughness might be due to some chemical reactions such as oxidation with soluble oxygen. In addition, it is expected that amorphous layers are thickly formed in the surface of 3-years ones.

![Figure 1](image)

Figure 1. SEM images of (a) pristine C\textsubscript{60}NWs, and (b) 3-years C\textsubscript{60}NWs that were formed when pristine ones were kept in the growth solution for more than 3 years.

![Figure 2](image)

Figure 2. Time evolution of XRD pattern during the drying in air for (a) pristine C\textsubscript{60}NWs and (b) 3-years C\textsubscript{60}NWs that were formed when pristine ones were kept in the growth solution for more than 3 years. (a) and (b) also include XRD patterns after drying in a vacuum. The XRD patterns were obtained with 0.1542 nm of Cu K\textalpha.

For the pristine and 3-years ones, time evolution of XRD pattern during the drying was measured as shown in figure 2(a) and 2(b), respectively. As shown in figure 2(a), for pristine C\textsubscript{60}NWs, XRD pattern taken for 25 min after the sampling from the glass bottles showed sharp peaks. The peaks were indexed by a hexagonal system with lattice constants of \(a=2.43\) nm and \(c=1.01\) nm (\(a/c=2.41\)). The hexagonal peaks are also in good agreement with those of C\textsubscript{60} solvated structure as reported previously [5]. The hexagonal solvated structure for 25 min can correspond to pristine ones in the growth solution.
As shown in figure 2(a), these sharp peaks were observed even after air-drying for 230 min. In the XRD pattern for 230 min, the broad peaks were also appeared at similar positions to those for the intrinsic C\textsubscript{60} crystals, and indexed by a fcc system with a lattice constant of \(a=1.44\) nm. Note that the peak broadening is due to the lowering of crystal quality for dried ones. In addition, almost all hexagonal peaks disappeared after drying in a vacuum so that only fcc broad peaks were observed as shown in figure 2(a). This indicates that the hexagonal solvated structure in pristine C\textsubscript{60}NWs is easily changed into the fcc, by drying. Such a change in the structure is due to the evaporation of solvent molecules in air or a vacuum. Similar change has been also observed in previous reports [5,6].

Figure 2(b) shows the time evolution of XRD pattern of 3-years ones during the drying. The XRD pattern taken for 30 min in air exhibits the peaks corresponding to the hexagonal solvated structure in pristine ones for 25 min in figure 2(a). The peaks were indexed by a hexagonal system with lattice constants of \(a=2.41\) nm and \(c=1.01\) nm (\(a/c=2.39\)). The lattice constant of a-axis is slight small compared with that of pristine ones as mentioned above. It should be noticed that no significant change in the XRD pattern was observed even after air-drying for 210 min as seen in figure 2(b). The hexagonal XRD pattern was also kept even after drying in a vacuum of \(10^{-5}\) Pa for 4 hours. Therefore, the hexagonal solvated structure for 3-years ones is kept even in air or a vacuum. In addition, no peak broadening for 3-years ones was observed with drying. This means that the high quality of 3-years ones is kept even after drying. Such structural feature for 3-years ones is quite different from that for pristine ones as mentioned above. This can be attributed to the difficulty of the evaporation of solvent molecules due to the thicker amorphous layer formed in the nanowisker surface.

*Figure 3.* Time evolution of main Raman bands during in air for (a) pristine C\textsubscript{60}NWs and (b) 3-years ones that were formed when pristine ones were kept in the growth solution for more than 3 years. (a) and (b) also include Raman bands after drying in a vacuum. The Raman bands at 270, 494, and 1468 cm\(^{-1}\) can be associated with \(H_g(1)\) “squashing”, \(A_g(1)\) “breathing”, \(A_g(2)\) “pentagonal pinch” modes of C\textsubscript{60} molecules, respectively. The Raman spectra were taken with 1064 nm excitation.
The time evolution of the Raman spectra for pristine C$_{60}$NWs and 3-years ones during the drying was also measured to examine the intermolecular interaction in the growth solution and air. Figure 3 shows the time evolution of main Raman bands at 270, 494, and 1468 cm$^{-1}$, which can be associated with $H_\parallel(1)$ squashing, $A_g(1)$ breathing, $A_g(2)$ pentagonal pinch modes of C$_{60}$ molecules, respectively. It is known that the peak profile of $H_\parallel(1)$ for C$_{60}$ molecules is quite different from that for crystalline C$_{60}$. Namely, the peak for C$_{60}$ molecules can be fitted by one Lorentzian curve while that for the crystals is fitted by several curves. Such splitting in $H_\parallel(1)$ mode for the crystals should be attributed to the crystal field due to the regular molecular arrangement in the crystals.

As discussed above, C$_{60}$NWs for 25 min in air correspond to pristine ones in the growth solution, and have the hexagonal solvated structure. However, for the corresponding Raman spectrum for 25 min as shown in figure 3(a), no clear splitting in $H_\parallel(1)$ peak was observed. This means that pristine C$_{60}$NWs in the growth solution have a smaller crystal field, i.e. smaller intermolecular interaction although they have the regular molecular arrangement. The small crystal field would be due to the solvent molecules in the crystals. On the other hand, clear splitting in $H_\parallel(1)$ peak was observed for fcc dried ones after air-drying for 120 min or after drying in a vacuum as shown in figure 3(a). This can be attributed to the increase of the crystal field of fcc lattice due to the evaporation of solvent molecules in air or a vacuum. Moreover, it was found that the peak frequency of $A_g(1)$ was slightly up-shifted with drying. This can be also explained by the increase of the intermolecular interaction due to the evaporation of solvent molecules.

Figure 3(b) shows the time evolution of the Raman spectrum of 3-years ones during the drying. The frequency and shape of Raman peaks of 3-years ones taken for 30 min in air are similar to those of pristine ones for 30 min in air in figure 3(a). This shows that no strong chemical bond of C$_{60}$ with C$_{60}$ or others such as solvents is formed even for 3-years ones, as pristine ones. Moreover, no change in the frequency and shape of all peaks for 3-years ones was observed even after air-drying for 150 min or after drying in a vacuum of $10^{-5}$ Pa for 4 hours. This means that 3-years ones in air and a vacuum can maintain the same intermolecular interaction as that in the growth solution. Such a feature for 3-years ones is quite different from that of pristine ones as mentioned above. These Raman features in figure 3 are also strongly correlated with those of XRD in figure 2.

**Figure 4.** Successive pictures of the bending deformation in air for a 3-years C$_{60}$NW that was formed when pristine one was kept in the growth solution for more than 3 years. The pictures show (a) straight one before applying a stress, (b) bent one with a curvature of 80 μm by applying a stress, and (c) straight one recovered after freeing from a stress, respectively. Note that the stress was manually applied to the tip of specimen with a needle as seen in (b).

For 3-years ones, the bending experiments were carried out in air. Figure 4 shows the successive pictures of the bending behavior of a 3-years one which has 500 nm in diameter and more than 100 μm in length. The straight one before applying a stress is indicated by the arrow in figure 4(a). According to the previous report [6], a wind pressure with a fan led to the break of pristine C$_{60}$NWs in air. However, 3-years ones in air were not broken by the same wind pressure as the previous one. This
means that 3-years ones have high strength even in air, at least compared with pristine ones as reported previously [6]. In order to apply larger stress, the tip of specimen was manually pushed by using a needle. Consequently, the bending deformation clearly occurred. Namely, the 3-years one was bent with a curvature of 80 μm, as shown in figure 4(b). The curvature is smaller than that for pristine ones in the solution [6]. Freeing from the stress, it almost recovered to original shape although a small plastic deformation occurs, as shown in figure 4(c). Such behavior of the bending shows that 3-years ones exhibit large elastic deformation even in air, as that in pristine ones in the growth solution [6]. This is because the hexagonal solvated structure for the 3-years ones is kept even in air or a vacuum. In addition, the toughness might be attributed to the thicker amorphous layer in the surface of 3-years ones.

4. Conclusion

C_{60}NWs are modified when pristine ones grown by a liquid-liquid interfacial precipitation method are kept in the growth solution for more than 3 years. The modified ones have the hexagonal solvated structure not only in the solution but also in air or a vacuum. The modified ones exhibit high strength and large elastic deformation even in air, quite differing from the brittle in pristine ones in air. The production of such toughened C_{60}NWs might lead to a breakthrough for the practical applications.

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References

[1] Miyazawa K, Kuwasaki Y, Obayashi A and Kuwabara M 2002 J. Mater. Res. 17 83-88
[2] Tachibana M, Kobayashi K, Uchida T, Kojima K, Tanimura K and Miyazawa K 2003 Chem. Phys. Lett. 374 279-285
[3] Asaka K, Kato R, Miyazawa K and Kizuka T 2006 Appl. Phys. Lett. 89 071912
[4] Ogawa K, Kato T, Ikegami A, Tsuji H, Aoki N, Ochiai Y and Bird J P 2006 Appl. Phys. Lett. 88 112109
[5] Minato J and Miyazawa K 2005 Carbon 43 2837-2841
[6] Watanabe M, Miyazawa K, Kojima K and Tachibana M 2008 IEEJ Trans. SM 128 321-324
[7] Kobayashi K, Tachibana M and Kojima K 2005 J. Cryst. Growth 274 617-621