Bending Deformation of C₆₀ Nanowhiskers in Solution and Air

Mami Watanabe Non-member (Yokohama City University)

Kun'ichi Miyazawa Member (National Institute for Materials Science)

Kenichi Kojima Non-member (Yokohama City University)

Masaru Tachibana Member (Yokohama City University)

Keywords : C₆₀ nanowhiskers, mechanical property, raman spectroscopy

C₆₀ nanowhiskers (C₆₀NWs) have been grown in solution by liquid-liquid interfacial precipitation method. The typical C₆₀NWs are less than 0.5 μm in diameter and more than 100 μm in length. The unique shapes of C₆₀NWs are attractive for the applications to nanoscale devices. However, almost all studies on the physical properties have been carried out in air or vacuum.

It is known that the structure of C₆₀NWs in air or vacuum is different from original one grown in solution. The C₆₀NWs in solution have a hexagonal solvated structure. The solvated structure rapidly changes into a face-centered-cubic (fcc) structure by the drying, i.e. the evaporation of solvent molecules in air or vacuum. Therefore, it is of interest to know what C₆₀NWs in solution show physical properties. In this paper, we report the mechanical property of C₆₀NWs in solution and air.

The mechanical properties of C₆₀ nanowhiskers in solution and air were investigated by the bending deformation. The bending deformation was carried out by applying wind pressure. The observation of the bending behavior was carried out in-situ by an optical microscope with a charge coupled device.

Fig. 1 shows the successive pictures of the bending behavior of a C₆₀NW in solution. The straight C₆₀NW before applying wind pressure is indicated by arrow in Fig. 1(a). The C₆₀NW was bended with wind pressure and reached the curvature of 290 μm, as shown in Fig. 1(b). Freeing from the wind pressure, the C₆₀NW recovered to original straight shape, as shown in Fig. 1(c). Such behavior of the bending show that C₆₀NWs in solution exhibit large elastic deformation.

The bending experiments were also carried out for C₆₀NWs in air. The C₆₀NW was bended under wind pressure, similar to C₆₀NWs in solution. However, the C₆₀NW in air was broken just after it was bended with the curvature of only 650 μm. This indicates that C₆₀NWs in air exhibit smaller elastic deformation, i.e. relatively brittle, compared with that in solution. It is obvious that C₆₀NWs in solution show abnormal large elastic deformation. This might be due to the solvated structure with weak intermolecular interaction for C₆₀NWs in solution.

From the analysis of the bending, the yield stress, or breaking strength, of C₆₀NWs in air was estimated. The yield stress, or breaking strength, σ for whiskers can be given by

$$\sigma = E \frac{r}{\rho} \quad (1)$$

where E is the Young modulus of whisker, r is the radius of

Fig. 1. Successive pictures of the bending deformation of a C₆₀NW in solution by wind pressure. The pictures show (a) straight one before applying wind pressure, (b) bended one with the curvature of 290 μm by wind pressure, and (c) straight one recovered after freeing from the wind pressure, respectively

whisker, and ρ is the curvature of the bending just before yielding. Eq. (1) was used for C₆₀NWs with the diameter of 500 nm and the curvature of 650 μm just before breaking in air. In addition, the Young's modulus of C₆₀NWs in air can be assumed to be 20 GPa corresponding to that of C₆₀ bulk crystals, since C₆₀NWs in air have fcc structure similar to that of the C₆₀ bulk crystals. Substituting these values into eq. (1), the yield stress, or breaking strength, of C₆₀NWs in air was estimated to be 7.7 MPa. This value is large by one order compared with 0.7 MPa in C₆₀ bulk crystals as has reported previously.

Bending Deformation of C₆₀ Nanowhiskers in Solution and Air

Mami Watanabe*	Non-member
Kun'ichi Miyazawa**	Member
Kenichi Kojima*	Non-member
Masaru Tachibana*	Member

The mechanical properties of C₆₀ nanowhiskers (C₆₀NWs) grown in a solution by a liquid-liquid interfacial precipitation method were investigated by a bending method. C₆₀NWs in the solution exhibited large elastic deformation where they recovered for large bending with a curvature of 290 μm . On the other hand, C₆₀NWs in air were broken even for small bending with only a 650 μm curvature. From the analysis of the bending, the yield stress or breaking stress for C₆₀NWs in air is estimated to be 7.7 MPa, that is larger by one order compared with 0.7 MPa for bulk C₆₀ crystals. In addition, it is shown that the Young's modulus for C₆₀NWs in the solution is 8.9 GPa, that is below a half of 20 GPa for bulk C₆₀ crystals.

Keywords : C₆₀ nanowhiskers, mechanical property, raman spectroscopy

1. Introduction

Solution-grown C₆₀ crystals have various structures and shapes that depend on organic solvent, growth temperature and so on. Recently, a new type of C₆₀ needle-like crystals called C₆₀ nanowhiskers (C₆₀NWs) were obtained in a solution by a liquid-liquid interfacial precipitation (LLIP) method, where they nucleate at the interface between a toluene solution of C₆₀ and isopropyl alcohol⁽¹⁾. Typical C₆₀NWs are less than 500 nm in diameter and more than 100 μm in length. The high aspect ratio of C₆₀NWs with the small diameter is very unique, compared with those of any needle-like C₆₀ crystals reported previously.

From the structural characterization by high resolution transmission electron microscopy, it was found that C₆₀NWs have a face-centered cubic (fcc) structure similar to that of intrinsic C₆₀ crystals and their growth direction corresponds to a [110] close-packed direction⁽¹⁾. In addition, Raman scattering measurements have shown that C₆₀NWs are condensed with weak van der Waals (vdW) forces and are easily polymerized under laser irradiation⁽²⁾. Such shapes and structural characteristics of C₆₀NWs may provide us with various applications such as nano-scale electronic devices and field emitters.

Some interesting physical properties, e.g. mechanical⁽³⁾ and electrical properties⁽⁴⁾, of C₆₀NWs have been also reported. However, most of such previous characterizations of C₆₀NWs were carried out for dried specimens in air or a vacuum. C₆₀ molecules should be solvated when they are in the growth solution. More recently, it has been reported that the structure of C₆₀NWs in air or a vacuum is different from that of original one grown in the solution⁽⁵⁾. C₆₀NWs in the solution have a hexagonal solvated structure and their growth direction corresponds to a [0001] direction. The hexagonal solvated structure rapidly changes into

the fcc structure by drying, i.e. the evaporation of solvent molecules in air or a vacuum. It is expected that the physical properties of C₆₀NWs in the solution are different from those in air or a vacuum. In this paper, we report the bending properties of C₆₀NWs in a solution and air.

2. Experimental Procedure

C₆₀NWs were grown by the LLIP method in below procedure as reported previously⁽⁶⁾. As-received C₆₀ powder (>99.98 %) was used as a source material. The saturated solution of C₆₀ and toluene was prepared and poured into a glass bottle (13.5 ml). Then, the isopropyl alcohol was gently added into the bottle to form a liquid-liquid interface, where the upper phase is isopropyl alcohol and the lower phase is a toluene solution of C₆₀. The bottle was loosely capped and kept under illumination at 294 K. The nucleation of C₆₀NWs can mainly occur at the liquid-liquid interface. The interface disappears due to the natural diffusion of the solution within 24 hours. After the disappearance of the interface, the growth rather than the nucleation can mainly occur. C₆₀NWs grown for more than one month exceed 1 mm in length but are still below 500 nm in diameter. These specimens were used for the measurements.

The LLIP method included some C₆₀ bulk crystals as impurities. They predominantly contribute to X-ray diffraction (XRD) and Raman spectra. To obtain intrinsic XRD and Raman spectra of C₆₀NWs, as-grown crystals were purified by several filtrations and then highly condensed by the centrifugation. The collective C₆₀NWs as shown in Fig. 1 were used in XRD and Raman measurements.

The structure and intermolecular interaction of C₆₀NWs were examined by XRD (RINT X-ray Diffractometer, Rigaku) and Raman spectroscopy (IFS 66v/S, FRA 106/S, Bruker). To confirm these features in the growth solution and air, the time evolution of the XRD and Raman spectra of C₆₀NWs during the drying was measured. In the measurements, the specimens were mounted on a glass sample holder immediately after the sampling from the growth solution. XRD patterns were obtained with a 0.1542 nm of Cu K α . The Raman spectra were taken with a 1064 nm excitation

* International Graduate School of Arts and Sciences, Yokohama City University,
22-2 Seto, Kanazawa-ku, Yokohama 236-0027

** Fullerene Engineering Group, Advanced Nano Materials Laboratory, National Institute for Materials Science
1-1 Namiki, Tsukuba, Ibaraki, 305-0044

Fig. 1. Collective C_{60} nanowhiskers (C_{60} NWs), purified by several filtrations and then condensed by the centrifugation. Note that it is difficult to observe C_{60} NWs individually since they are highly condensed.

from a YAG laser in order to avoid the photo-polymerization of C_{60} by excitation.

The mechanical properties of C_{60} NWs in the solution and air were investigated by a bending method. To observe the bending behavior in the solution, the specimens were mounted on the glass plate with droplets, from the growth solution. The bending deformation for both specimens in the solution and air was carried out by applying a wind pressure with a fan. The wind pressure or the stress applied to C_{60} NWs 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. Result and Discussion

Fig. 2 shows the time evolution of XRD pattern of C_{60} NWs during the drying process. The XRD pattern taken for 25 min after the sampling from the glass bottles showed sharp peaks. The sharp peaks were observed for up to 230 min whereas the broad peaks were at the similar positions as those for the intrinsic C_{60} bulk crystals and indexed by the fcc system with a cell dimension of $a=1.44$ nm. This indicates that the structure was changed into the fcc, from a solvated structure by the evaporation of solvent molecules in air. The pattern taken for 25 min in Fig. 2 were indexed by the hexagonal system with cell dimensions $a=2.43$ nm and $c=1.01$ nm ($a/c=2.41$). Such a change in structure by drying is similar to that as has been reported previously.

The time evolution of the Raman spectrum of C_{60} NWs during the drying was also measured to examine the intermolecular interaction in C_{60} NWs in the solution and air. Fig. 3 shows the time evolution of main Raman bands at 270, 495, and 1468 cm^{-1} in air, which can be associated with $H_g(1)$ squashing, $A_g(1)$ breathing, $A_g(2)$ pentagonal pinch modes of C_{60} molecules, respectively. For the comparison, Raman bands in C_{60} molecules in a toluene solution, the hexagonal C_{60} bulk crystals grown from a toluene solution, and fcc C_{60} bulk crystals grown from sublimation are included in Fig. 3.

No significant change in the peak profiles of $A_g(1)$ and $A_g(2)$ modes is observed although the frequencies of the peaks are shifted. On the other hand, the peak profile of $H_g(1)$ for C_{60} molecules is quite different from that for the crystalline C_{60} . Namely, the peak for C_{60} molecules was fitted by a Lorentzian curve while that for the crystals can be fitted by several curves. Such splitting in $H_g(1)$ mode for the crystals should be attributed to crystal field due to regular molecular arrangement in the

Fig. 2. Time evolution of XRD pattern for C_{60} NWs during the drying process (a). The XRD pattern for intrinsic C_{60} bulk crystals with the fcc structure grown by sublimation (b) is included in the figure. The XRD patterns were obtained with 0.1542 nm of Cu $K\alpha$.

Fig. 3. Time evolution of main Raman bands for C_{60} NWs during the drying process (a). The Raman bands at 270, 495, and 1468 cm^{-1} can be associated with $H_g(1)$ “squashing”, $A_g(1)$ “breathing”, $A_g(2)$ “pentagonal pinch” modes of C_{60} molecules, respectively. For the comparison, Raman bands in C_{60} molecules in a toluene solution (b), the hexagonal C_{60} bulk crystals grown from a toluene solution (c), and the fcc C_{60} bulk crystals grown from sublimation (d) are included in the figure. The Raman spectra were taken with 1064 nm excitation.

Fig. 4. Successive pictures of the bending deformation of a C₆₀NW in the solution by a wind pressure. The pictures show (a) straight one before applying a wind pressure, (b) bent one with a curvature of 290 μm by a wind pressure, and (c) straight one recovered after freeing from a wind pressure, respectively.

crystals. C₆₀NWs in the solution have the hexagonal structure which is similar to that of C₆₀ bulk crystals grown from a toluene solution. However, no clear splitting in H_g(1) peak was observed for C₆₀NWs in the solution. This means that C₆₀NWs in the solution have a smaller crystal field, i.e. smaller intermolecular interaction although they have a regular molecular arrangement, similar to that of C₆₀ bulk crystals. It is expected that such intermolecular interaction in C₆₀NWs with solvated structure can lead to unique physical properties differing from those in air.

For such C₆₀NWs in a solution and air, the bending deformation was investigated. Fig. 4 shows the successive pictures of the bending behavior of a C₆₀NW which has 500 nm in diameter and more than 100 μm in length. The straight C₆₀NW before applying a wind pressure is indicated by the arrow in Fig. 4(a). The C₆₀NW was bent with a wind pressure and reached a curvature of 290 μm, as shown in Fig. 4(b). Freeing from a wind pressure, the C₆₀NW recovered to original straight shape, as shown in Fig. 4(c). Such behavior of the bending shows that C₆₀NWs in the solution exhibit large elastic deformation.

The bending experiments were also carried out for C₆₀NWs in air, as shown in Fig. 5. A straight C₆₀NW before applying a wind pressure is indicated by the arrow in Fig. 5(a). The C₆₀NW was bent under a wind pressure, as shown in Fig. 5(b). However, the C₆₀NW in air was broken just after it was bent with a curvature of only 650 μm, as shown in Fig. 5(b). Therefore, C₆₀NWs in air exhibit smaller elastic deformation, i.e. are relatively brittle, compared with that in the solution. As clearly shown, C₆₀NWs in

Fig. 5. Successive pictures of the bending deformation of a C₆₀NW in air. The stress was applied by a wind pressure. The pictures show (a) straight one before applying a wind pressure, and (b) bent one with the curvature of 650 μm by a wind pressure, respectively. The further bending leads to the break of the C₆₀NW.

the solution show large elastic deformation. This might be due to the solvated structure of C₆₀NWs with weak intermolecular interaction.

The yield stress or breaking strength for whiskers can be estimated from loop-like deformation⁽⁷⁾. In the deformation, the curvature of the loop increases with stress, and further increases in stress leads to a yield or break of the whisker. The yield stress σ of the whisker can be estimated from the curvature just before yielding, and is given by

$$\sigma = E \frac{r}{\rho} \quad (1)$$

where E is the Young's modulus of whisker, r is the radius of whisker, and ρ is the curvature of the loop just before yielding⁽⁷⁾. Eq. (1) can be obtained from the theory on beam deformation with $r \ll \rho$. Therefore, Eq. (1) is available for C₆₀NWs with the diameter of 500 nm and the curvature of 650 μm just before breaking in air in Fig. 5(b). In addition, the Young's modulus of C₆₀NWs in air can be assumed to be 20 GPa corresponding to that of C₆₀ bulk crystals⁽⁸⁾, since C₆₀NWs in air have the fcc structure condensed with weak vdW interaction similar to that in C₆₀ bulk crystals as mentioned above. Substituting these values into Eq. (1), the yield stress or breaking strength for C₆₀NWs in air is estimated to be 7.7 MPa. This value is larger by one order compared with 0.7 MPa in C₆₀ bulk crystals as has been reported previously⁽⁹⁾.

Assuming that the yield stress (7.7 MPa) for C₆₀NW in air as mentioned above is similar to the stress applied to C₆₀NW in the solution in Fig. 4, a Young's modulus of C₆₀NWs in the solution can be also estimated by using Eq. (1). For the C₆₀NW with the diameter of 500 nm and the curvature of 290 μm in the solution in Fig. 4(b), the Young's modulus is estimated to be 8.9 GPa, that is

below a half of 20 GPa for C_{60} bulk crystals. In this experiment, it is difficult to obtain more reliable values since the stress applied to C_{60} NWs could not be measured. However, these values obtained in this paper are very important as reference data for further study of mechanical properties of C_{60} NWs and the applications.

4. Conclusion

We have shown in-situ observation of the bending deformation of C_{60} NWs in not only air but also solution. It was shown that C_{60} NWs in the solution exhibit large elastic deformation compared with that in air. Such elastic property of C_{60} NWs with solvated structure might lead to new applications.

Acknowledgement

This work was supported by a Strategic Research Project (K19044) in Yokohama City University.

(Manuscript received Nov. 28, 2007, revised Apr. 1, 2008)

References

- (1) K. Miyazawa, Y. Kuwasaki, A. Obayashi, and M. Kuwabara : "C₆₀ nanowhiskers formed by the liquid-liquid interfacial precipitation method", *J. Mater. Res.*, Vol.17, pp.83-88 (2002)
- (2) M. Tachibana, K. Kobayashi, T. Uchida, K. Kojima, K. Tanimura, and K. Miyazawa : "Photo-assisted growth and polymerization of C₆₀ nanowhiskers", *Chem. Phys. Lett.*, Vol.374, pp.279-285 (2003)
- (3) K. Asaka, R. Kato, K. Miyazawa, and T. Kizuka : "Buckling of C₆₀ whiskers", *Appl. Phys. Lett.*, Vol.89, pp.071912-1-071912-3 (2006)
- (4) K. Ogawa, T. Kato, A. Ikegami, H. Tsuji, N. Aoki, and Y. Ochiai : "Electrical properties of field-effect transistors based on C₆₀ nanowhiskers", *J.P. Bird, Appl. Phys. Lett.*, Vol.88, pp.112109-1- 112109-3 (2006)
- (5) J. Minato and K. Miyazawa : *Carbon*, "Solvated structure of C₆₀ nanowhiskers", Vol.43, pp.2837-2841 (2005)
- (6) K. Kobayashi, M. Tachibana, and K. Kojima : "Photo-assisted growth of C₆₀ nanowhiskers from solution", *J. Cryst. Growth*, Vol.274, pp.617 (2005)
- (7) T. Kaneko : "Whiskers", Kyouritsu Shuppan, Tokyo (1993)
- (8) M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund : "Science of Fullerenes and Carbon Nanotubes", Academic Press, New York (1996)
- (9) T. Komatsu, M. Tachibana, and K. Kojima : Plastic deformation of C₆₀ single crystals", *Phil Mag.*, Vol.81, pp.659-666 (2001)

Mami Watanabe

(Non-member) was born in 1985. She received B.S. in 2007 from Yokohama City University. She is now a graduate student of master course of Graduate School of Yokohama City University (Tachibana Lab)

Kun'ichi Miyazawa

(Member) was born in 1955. He received D.E. degree from The University of Tokyo in 1987. He was a lecturer of School of Engineering, The University of Tokyo from 1989 to 2002, and moved to National Institute for Materials Science in 2002. He is now engaged in the synthesis, characterization and application of low-dimensional fullerene materials such as fullerene nanowhiskers, fullerene nanotubes and fullerene nanosheets.

Kenichi Kojima

(Non-member) was born in 1942. He received D.E. degree from Tohoku University in 1971. He is now a professor of Yokohama City University.

Masaru Tachibana

(Member) was born in 1963. He received D.E. degree from Waseda University in 1995. He is now a professor of Yokohama City University. His research interests are the physical properties of various kinds of molecular crystals composed of small molecules to giant ones such as proteins. Current research projects involve the development of synthesis and crystal growth of novel materials such as carbon nanotubes and fullerenes.