Hindawi Publishing Corporation
Journal of Nanotechnology
Volume 2012, Article ID 583817, 5 pages
doi:10.1155/2012/583817

Research Article

Solvation-Assisted Young's Modulus Control of Single-Crystal Fullerene C_{70} Nanowhiskers

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Received 6 June 2011; Accepted 31 October 2011

Academic Editor: Zheng Hu

Single-crystal nanowhiskers (NWs) composed of fullerene C_{70} molecules were synthesized by the liquid-liquid interfacial precipitation method that used *m*-xylene as a saturated solution of C_{70} molecules. Bending behavior of the individual NWs was observed by *in situ* transmission electron microscopy equipped with nanonewton force measurements using an optical deflection method. The Young's modulus of the NWs was estimated to be 0.3–1.9 GPa, which was 2–7% of the moduli of fullerene NWs with similar diameters synthesized using other solvents, that is, toluene and pyridine. The influence of the solvent used in the precipitation method on Young's modulus is discussed.

1. Introduction

Crystals composed of fullerene molecules have been synthesized by precipitation methods [1–13]. The crystals show various morphologies, that is, plates, films, and rods. In particular, Miyazawa et al. discovered the one-axis preferential growth of fullerene single crystals; a liquid-liquid interfacial precipitation (LLIP) method produces fullerene nanowhiskers (NWs) and nanotubes (NTs) with high length-to-diameter aspect ratios [14]. Because this structural feature is suitable for application in advanced nanodevices, the mechanical properties of these NWs and NTs have been the focus of a considerable amount of research. *In situ* transmission electron microscopy (TEM) equipped with piezomanipulation of individual NWs and NTs enables investigating the mechanical properties of such nanometer-sized materials [15–18].

The Young's moduli of fullerene NWs and NTs have been estimated by this method [19–22]. The structures of fullerene NWs and NTs synthesized by LLIP methods are influenced by solvation behaviors, suggesting that the mechanical properties depend on the solvents used. Two solvents, that is, toluene and pyridine, have been intensively used for the synthesis of NWs and NTs owing to their high productivity rates. In this study, we synthesized C_{70} NWs by the LLIP method using another solvent (*m*-xylene) and investigated their mechanical properties by *in situ* TEM.

2. Experimental

A saturated solution of C_{70} molecules in *m*-xylene was poured into isopropyl alcohol, followed by precipitation of C_{70} NWs. Then, the solution was added dropwise to an edge of a gold plate. The plate was mounted onto a specimen holder of the transmission electron microscope equipped with a piezomanipulation system at the University of Tsukuba [23–26]. A silicon microcantilever with a nanometer-sized tip that is used for contact-type atomic force microscopy was fixed onto a cantilever holder. Both the specimen and the cantilever holders were inserted in the microscope. The cantilever tip was brought into contact with individual NWs fixed on the plate edges by the piezomanipulation system of the microscope. The tip was then pressed

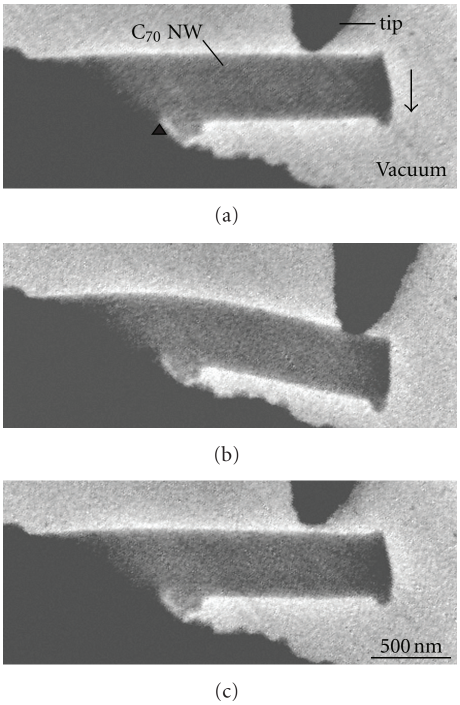

Figure 1: Time-sequence series of bright-field images of cantilever-beam-type loading, which causes bending of the C_{70} single-crystal nanowhisker with outer diameter of 410 nm. The left side of the nanowhisker is fixed onto a gold plate. The arrow indicates the loading direction of the cantilever tip for atomic force microscopy. The fulcrum is indicated by the triangle. This bending test was performed in the vacuum.

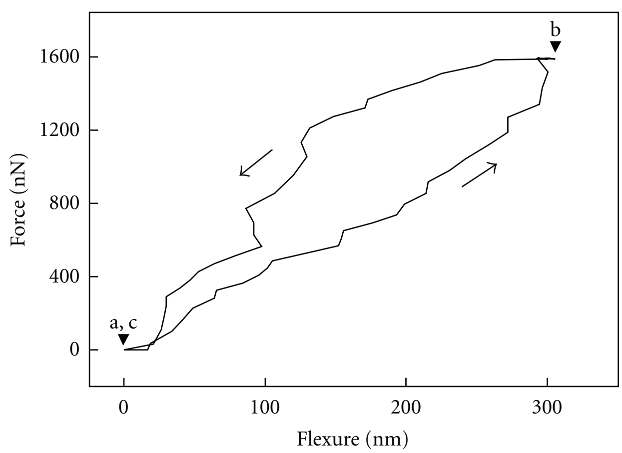

Figure 2: Force-flexure curve of C_{70} nanowhisker during bending shown in Figure 1. Points a–c correspond to the states shown in Figures 1(a)–1(c), respectively. The arrows indicate the time path of recording.

on the NWs for bending with cantilever beam-type loading. The cantilever tip was then pulled back to release the force. A series of such manipulations was performed several times for the same NW at room temperature in a vacuum of 1×10^{-5} Pa. The deformation process was observed *in situ* using a video capture system using a charge-coupled device camera with a time resolution of 17 ms. Simultaneously, the force applied on the NWs was measured by an optical detection of the cantilever deflection used in atomic force microscopy. The spring constant of the cantilever was measured to be 4.7 N/m.

3. Results

Figures 1(a)–1(c) show a time-sequence series of the bright-field images of the bending process of a C_{70} NW protruding from an edge of the gold plate. The dark triangular region in the upper part of each frame is the cantilever tip. The brighter region around the NW is the vacuum. The outer diameter of the NW is 410 nm, and the length of the deformed portion is 1.2 μm. The crystal structure of the NT was tetragonal. This crystal structure has been observed in dried C_{60} NWs and NTs synthesized by LLIP methods [17–19]. This structure arises from polymerization of fullerene molecules [27]. The longer growth axis of the NW is aligned parallel to [110]. The left side of the NT in Figure 1 was fixed on the gold plate. In the bending test, the cantilever tip was initially placed in contact with the NW (Figure 1(a)). Then, the NT was pressed along the direction indicated by the arrow in Figure 1(a) to cause bending (Figure 1(b)). Subsequently, the tip was released, and the NT recovered its initial straight shape as in Figure 1(c). Thus, this bending behavior corresponds to an elastic deformation.

Figure 2 shows the relationship between the force and flexure during the bending process shown in Figure 1. The points indicated by arrowheads a–c in Figure 2 correspond to the TEM images in Figures 1(a)–1(c). The maximum flexure and loading at the free end were 300 nm and 1590 nN, respectively. Hysteresis is observed in the curve in Figure 2 during the pressing and pulling process of the cantilever tip. It is attributed to the bonding of the cantilever tip with the NW surface [28]. The curve of the pressing process (a-b in Figure 2) can be approximated by one linear component. On the other hand, the curve of the pulling process (b-c in Figure 2) is a sequence of several linear slopes. The slope of the pulling process near point c is similar to that of the pressing process. Thus, we used this slope for the estimation of the Young's modulus of the NW. On the basis of the relationship among force, flexure, and Young's modulus for cantilever-beam loading in standard mechanics of materials, the Young's modulus of the NWs was estimated to be 1.9 ± 0.1 GPa. We performed bending tests with the same type of loading for other NWs with the outer diameters of 580 nm and 770 nm. Their Young's moduli were estimated to be 1.1 ± 0.3 GPa and 0.3 ± 0.3 GPa, respectively.

Figure 3 shows the relationship between the Young's modulus and the outer diameter of the C_{70} NWs. Note that the Young's modulus increases as the outer diameter decreases. The relationship is well fitted by a straight line.

4. Discussion

The Young's moduli of single-crystal C_{60} and C_{70} particles, films, NWs, and NTs previously reported are shown

Table 1: Young's modulus of fullerene crystals (NW: nanowhisker; NT: nanotube).

Shapes	Molecules	Young's modulus (GPa)	References
Particle	C_{60}	20 ± 5	Hoen et al. [34]
... (fcc [100])	...	8.3 ± 0.6	Kobelev et al. [35]
... (fcc [110])	...	13.2 ± 1	...
... (fcc [111])	...	16.3 ± 1.2	...
Film	...	9.99 ± 1.25	Fioretto et al. [36]
...	...	10	Kolomenskii et al. [32]
...	...	12 ± 1	Coufal et al. [37]
...	...	12.7	Murugavel et al. [33]
...	...	15.9	Shi et al. [7]
...	C_{70}	4 ± 1	Kolomenskii et al. [32]
...	...	8.7	Murugavel et al. [33]
NW (dia. 130 nm)	C_{60}	54 ± 3	Asaka et al. [15]
... (dia. 160 nm)	...	32 ± 6	...
... (dia. 420 nm)	...	28 ± 5	...
... (dia. 123 nm)	...	53–69	Saito et al. [18]
... (dia. 410 nm)	C_{70}	1.9 ± 0.1	The present study
... (dia. 580 nm)	...	1.1 ± 0.3	...
... (dia. 770 nm)	...	0.3 ± 0.3	...
NT (dia. 510 nm)	C_{60}	62–107	Kizuka et al. [17]
...(dia. 270 nm)	C_{70}	68–110	Kizuka et al. [38]
... (dia. 340 nm)	...	82 ± 5	...
... (dia. 470 nm)	...	61 ± 5	...

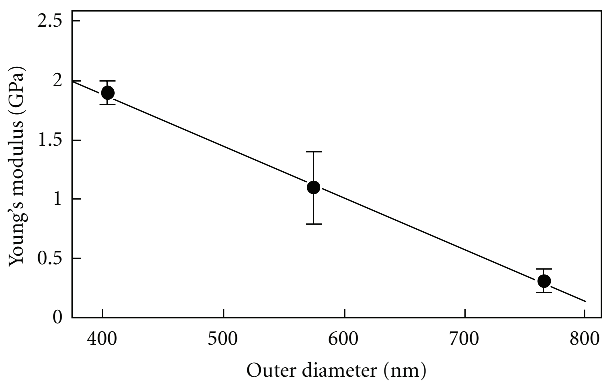

Figure 3: Young's modulus of C_{70} nanowhiskers plotted against the outer diameter. The solid line indicates linear approximation.

in Table 1. The NWs and NTs in previous studies were synthesized by the LLIP method using toluene and pyridine as solvents. The Young's modulus of the present C_{70} NWs synthesized by the LLIP method using *m*-xylene is 0.3–1.9 GPa. Because the Young's modulus of fullerene NWs depends on the outer diameter as shown in Figure 3 and in previous measurements [15, 17, 18], we compared the Young's modulus of the present C_{70} NWs with that of C_{60} NWs with similar outer diameters. The Young's modulus of the present C_{70} NW with an outer diameter of 410 nm is 7% of that of a C_{60} NW with an outer diameter of 420 nm. NTs have different structures from NWs, and the Young's modulus of C_{60} NTs is ~220% higher than that of C_{60} NWs as shown in Table 1. The ratio of the modulus of C_{70} NWs to C_{60} NTs becomes further lower; the Young's modulus of the C_{70} NW with an outer diameter of 580 nm is 2% of that of a C_{60} NT with an outer diameter of 510 nm. On the other hand, the modulus of the films in Table 1 indicates that by changing the constituent molecules from C_{60} to C_{70}, the modulus decreases only by 30–50%. This implies that the considerable decrease in the Young's modulus of the present NWs cannot be attributed to only the difference in constituent molecules. Therefore, the decrease in the Young's modulus in the present NWs is caused by the difference in solvents used in the LLIP.

During incubation, the crystal structures of fullerene NWs and NTs synthesized by the LLIP method using toluene and pyridine were investigated by Minato and Miyazawa [22]. Pristine NWs show solvated hexagonal structures that transform into face-centered cubic structures by desiccation. Thus, the solvents affect the molecular bonding, configuration, and defect formation in pristine NWs synthesized by LLIP methods. Strain, hollow spaces, or vacancy-cluster type defects are introduced when the molecules are disconnected by insertion of the solvents. It was also reported that stacking faults were formed in the fullerene crystals precipitated in *o*-xylene [29]. As a result, these defects lead to the formation of pores in NWs after desiccation. In particular, the density of pores is higher in the interior region around the center axis [30]. Ringor and Miyazawa proposed that NTs are formed by elution of the interior regions with defects [31].

As Saito et al. discussed, the decrease in Young's modulus of NWs with the outer diameter, which is observed in the present study, suggests the presence of defects in the interior regions [18]. The Young's modulus of fullerene films decreases as density decreases [32, 33]. Therefore, it is deduced that the *m*-xylene molecules remaining in the pristine NWs cause defects in the interior regions after desiccation, leading to the considerable decrease in Young's modulus.

5. Conclusion

Using *in situ* TEM, we performed bending tests on individual single-crystal C_{70} NWs synthesized by the LLIP method using *m*-xylene as the solvent. The Young's modulus of the NWs was estimated to be 0.3–1.9 GPa, which is 2–7% of the moduli of fullerene NWs and NTs with similar diameters synthesized using toluene and pyridine as solvents. It was inferred that the considerable decrease in Young's modulus was caused by the higher number of defects in the interior regions introduced by solvation of *m*-xylene in the pristine NWs. This result reveals that the Young's modulus of NWs can be controlled to a double-digit magnitude by appropriate selection of solvents, leading to design of structural materials using NWs.

Acknowledgment

This study was partly supported by Grants-in-Aid from the Ministry of Education, Culture, Sport, Science and Technology, Japan (nos. 22310065 and 23651127).

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