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# Dependency of Young's modulus on diameter in Crystalline $C_{70}$ Nanotubes

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## 1. Introduction

Miyazawa *et al*. synthesized single-crystal fullerene nanowhiskers (NWs) with a high aspect ratio of length to diameter [1]. Recently, they also found that tubular fullerene NWs, i.e., fullerene-crystal nanotubes (NTs), were synthesized by the same method [2, 3]. The mechanical properties of NTs have been investigated to apply them. Saito *et al.* performed buckling tests of $C_{60}$ NTs by *in situ* transmission electron microscopy (TEM) and estimated their Young's modulus: 62–107 GPa [4]. In this paper, to investigate the mechanical nature of fullerene NTs of another well-known fullerene molecule, i.e., $C_{70}$, we performed bending tests for them by *in situ* TEM.

## 2. Method

We synthesized $C_{70}$ NTs by the liquid-liquid interfacial precipitation method using a saturated solution of $C_{70}$ molecules in pyridine and isopropyl alcohol [2]. The solution including precipitated FNTs was dropped on the tip of a gold plate. The tip was mounted on a specimen holder of the microscope equipped with a piezomanipulation system in the University of Tsukuba. A silicon microcantilever with a nanometer-sized needle tip for atomic force microscopy was fixed on a cantilever holder. Both the specimen and cantilever holders were inserted into the microscope. Then we deformed individual $C_{70}$ NTs using the cantilever tip at room temperature in a vacuum of $1 \times 10^{-5}$ Pa. The deformation process was observed *in situ* using a television capture system. Simultaneously, the force acting on the NTs was measured by an optical detection of the cantilever deflection.

## 3. Results and discussion

Figures 1(a)–1(c) show a time-sequence series of bright-field images of the bending process of a $C_{70}$ NT protruding from an edge of the gold plate. The outer and inner diameters of the NT are 340 nm and 80 nm, respectively. The dark triangular region in the upper part in each frame of Fig. 1 is the cantilever tip. The length of the deformed part is 3.5 μm. The brighter region around the NT is the vacuum. The crystal structure of the NT was the tetragonal with lattice constants of $a = 1.48 \pm 0.03$ nm and $c = 1.69 \pm 0.04$ nm. The longer growth axis of the NT is aligned parallel to [110]. The averaged center-to-center distance between adjoining $C_{70}$ molecules in the NT along the growth direction is 3% smaller than that of $C_{70}$ NTs with a face-centered-cubic structure [2]. According to Miyazawa *et al*., this difference is attributed to polymerization of the molecules [5]. In the present bending test, first, the cantilever tip was placed in contact with the NT (Fig. 1(a)). Then, the NT was pressed along the direction indicated by the arrow in Fig. 1(a) and was bent (Fig. 1(b)). Subsequently, the tip was released, and the NT recovered its initial straight shape (Fig. 1(c)). Thus, this

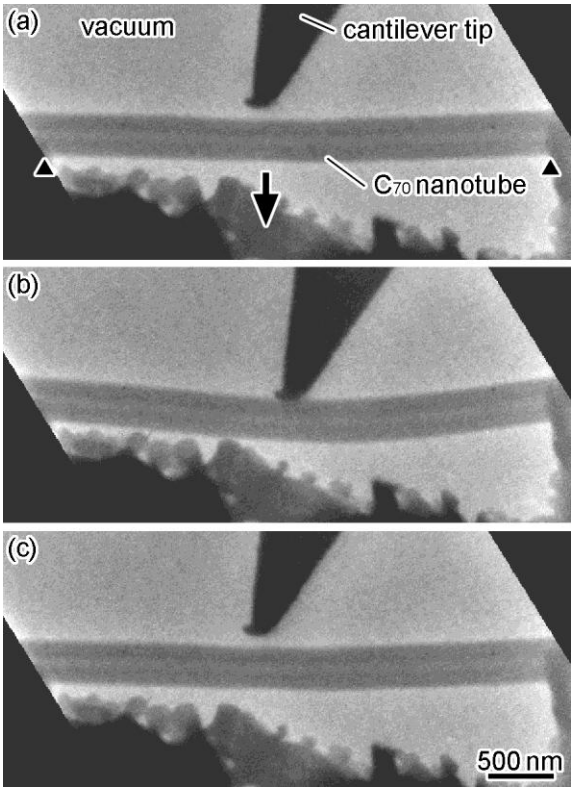


**Fig. 1.** Time-sequence series of bright-field images of elastic bending of $C_{70}$ NT. The two triangles indicate the fulcra during bending.

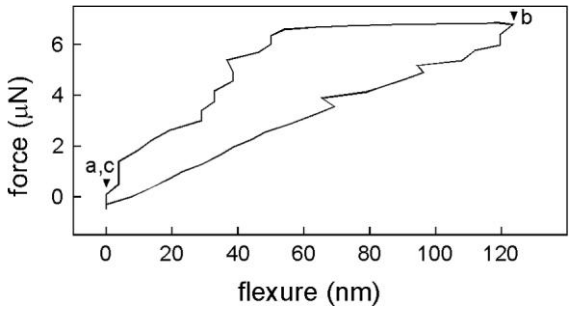


**Fig. 2.** Force-flexure curve of $C_{70}$ NT for bending process presented in Fig. 1.

observation shows that the bending is an elastic deformation. This bending recovery cycle was repeated several times for the same NT. Figure 2 shows the relationship between the force and the flexure. The points indicated by arrowheads a–c correspond to the TEM images presented in Figs. 1(a)–1(c). From this *in situ* bending test, we estimated the Young's modulus of the NTs to be 82±5 GPa. We performed the bending test for other NTs which diameters are 270 nm and 470 nm Their Young's moduli were estimated to be 68–110 GPa and 61±5 GPa, respectively. These values are 7–28 times larger than that of $C_{70}$ crystalline films (4–9 GPa) [6, 7]. From the result of structural analysis, we attribute the increase in Young's modulus observed in this study to an effect of the polymerization of the constituent $C_{70}$ molecules. In Fig. 3, we plotted the Young's modulus of the present $C_{70}$ NTs with previously reported values of $C_{60}$ NWs and $C_{60}$ NTs against their outer diameter [4, 8, 9, 11]. All of the Young's moduli of $C_{70}$ NTs are higher than these of $C_{60}$ NWs. Saito *et al.* proposed that the Young's modulus of NTs is higher than that of NWs because of the lack of their softer core parts [4]. However, compared with the Young's modulus of $C_{60}$ NTs which have similar diameters (500 nm), the modulus of $C_{70}$ NTs is lower. According to previous reports, the Young's modulus of $C_{70}$ crystals is

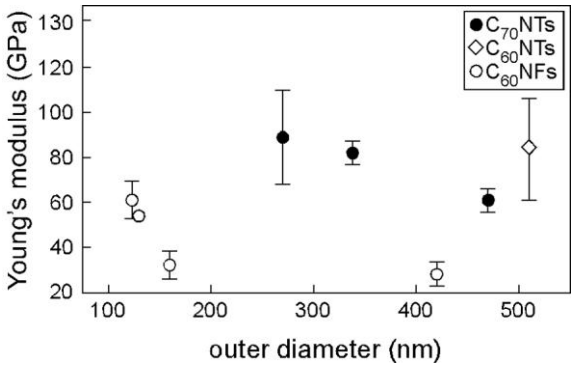


**Fig. 3.** Young's modulus of $C_{70}$ NTs, $C_{60}$ NTs and $C_{60}$ NWs.

lower than that of $C_{60}$ crystals [6, 7]. This is because that the most stable packing of the fullerene molecules in $C_{70}$ crystal has a lower density than for a $C_{60}$ crystal, as calculated by Quo *et al.*[10].

The Young's modulus of $C_{70}$ NTs increases as the outer diameter decreases. However, if NTs are composed of a single shell component, the Young's modulus of $C_{70}$ NTs would be constant regardless of their outer diameter. Then, it is proposed that their core regions partially remain, resulting in the formation of the tubular structures [2].

## 4. Conclusion

We performed bending tests of individual $C_{70}$ NTs by *in situ* TEM. From the measurements of the force-flexure relationships of the $C_{70}$ NTs, the Young's modulus was estimated to be 61–110 GPa. Because of the effect of polymerization of the constituent $C_{70}$ molecules, these values are larger than that of $C_{70}$ crystalline films $C_{60}$ NWs and $C_{60}$ NTs in similar diameters.

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