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In situ High-Resolution Transmission Electron Microscopy of Deformation of Multi-walled Carbon Nanometer-sized capsules

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1. Introduction

Since the fullerene C_{60} molecule was discovered, vari-ous kinds of nanometer-sized structure of carbon have been reported: multi- and single-walled nanotubes, on-ion-like shells, and corns [1-6]. We recently developed an experi-mental method to manipulate nanometer-sized car-bon tips inside a transmission electron microscope [7,8] and synthe-sized a nanometer-sized hollow-cage structure of carbon, i.e. multi-walled carbon nanocapsules [9]. In this paper, we demonstrated in situ atomistic observations of the deforma-tion of individual carbon nanocapsules with si-multaneous force measurement. The mechanical properties are analyzed based on the mechanics of materials at an atomic scale.

2. Experiment

We synthesized single crystalline whiskers composed of C_{60} molecules with sub-micrometer diameters by a liq-uid-liquid interfacial precipitation method using a tolu-ene solution saturated with fullerene powders of C_{60} - 0~3 mol% (η2-C_{60})Pt(PPh3)2 and isopropyl alcohol [10,11]. The crystalline C60 whiskers were heated in a high vacuum at 1373 K for 30 min to transform them into amorphous car-bon whiskers. The transformed whiskers were then dis-persed on the tip of a gold plate of 50 μm thickness. The gold plate was mounted on a specimen holder for a trans-mission electron microscope equipped with a force meas-urement system [7]. The nanometer-sized silicon tip of the cantilever, as used for atomic force microscopy, was coated with a gold film of 5 ~ 10 nm thickness, and was then fixed in front of a tube-type piezoelectric element on another specimen holder. The cantilever-tip was brought into con-tact with one of the amorphous carbon whiskers at every atomistic interval inside the microscope as shown in Fig. 1(a). We impressed a current into the whisker at room temperature in a vacuum of 1 x 10^{-5} Pa to synthesize multi-walled carbon nanometer-capsules aggregating to the whisker (Fig. 1(b)) [9]. We separated the cantilever-tip from the whisker and stopped the impression of current for the synthesis. We then picked up one of the nanocapsules (Fig. 1(c)), and pressed it into the surface of the gold plate using the cantilever-tip (Fig. 1(d)). The deformation was observed in situ by high-resolution transmission electron microscopy with a TV rate system. The microscope was operated at an acceleration voltage of 200 kV. The time-resolution of image observations was 17 ms. Varia-tions in force during deformation were measured at inter-vals of 4 ms by means of an optical cantilever method as used in atomic force microscopy.

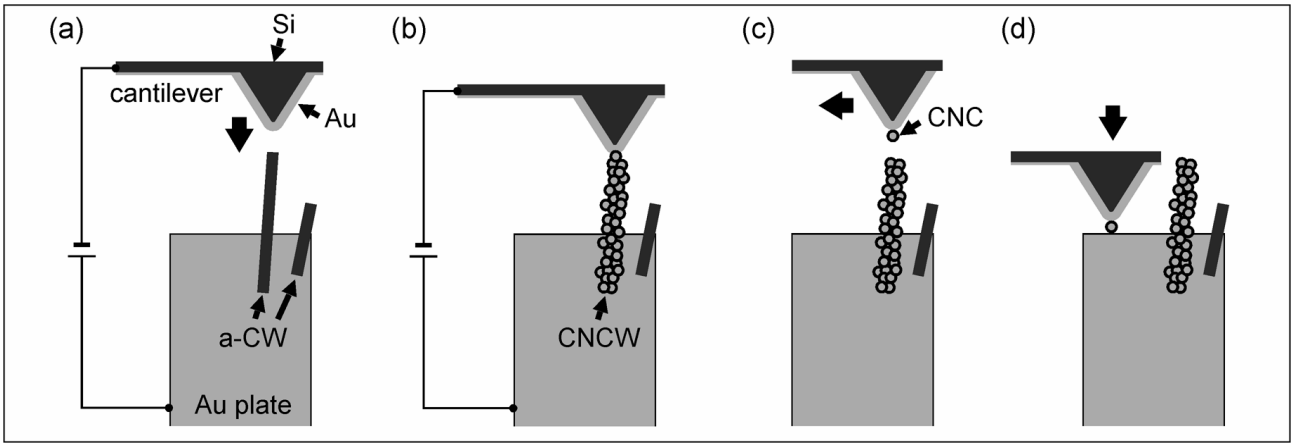

Fig. 1 Illustration of the operation procedure. (a) Contact of the cantilever-tip with one of amorphous carbon whiskers (a-CW). The can-tilever-tip was coated with a thin gold film. (b) Synthesis of the whisker composed of multi-walled carbon nanocapsules (CNCW) by impression of current. (c) Retraction of the cantilever-tip and transfer of one carbon nanocapsule (CNC) to the surface of the gold plate, and (d) compressive deformation.

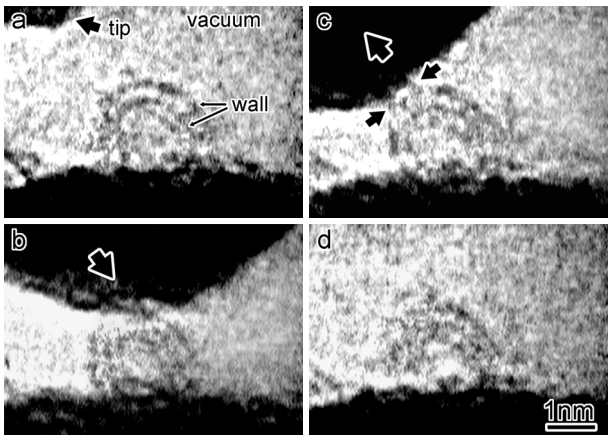

Fig. 2 Time-sequential high-resolution images of deformation of a multi-walled carbon nanocapsule of 2.50 ± 0.05 nm in diameter.

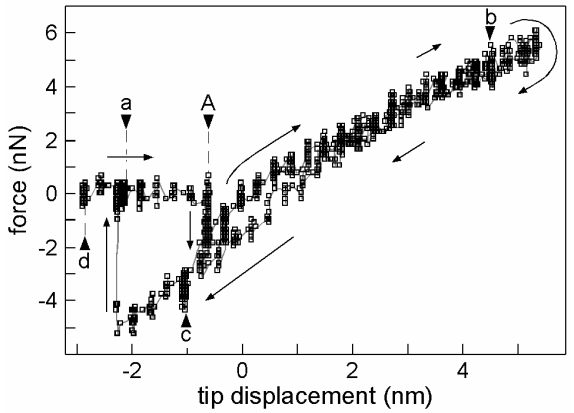

Fig. 3 Tip displacement-force curve during deformation in Fig. 2. At the arrowhead A, the cantilever-tip jumps to contact with the nanocapsule.

3. Results and Discussion

Figure 2 shows time-sequential high-resolution images of the deformation of the nanocapsule. The compression and retraction of the nanocapsule were repeated several times. The dark regions at the top and the bottom show the cantilever-tip and the surface of the gold plate, respectively. The bright regions are a vacuum. Figure 3 shows the rela-tionship between the displacement of the cantilever-tip and force during the deformation in Fig. 2. The points indicated by arrowheads a-d in Fig. 3 correspond to the times at which Figs. 2(a)-2(d) were observed. In Fig. 2(a), the width of the nanocapsule along the compressing direction is 2.50 ± 0.05 nm, and the walls have two atomic layers. When the distance between the cantilever-tip and the nanocapsule is reduced to 1.0 nm, the cantilever-tip jumps into contact with the surface of the nanocapsule. The attractive force at the jump is found to be 2.0 nN as shown by the arrowhead A in Fig. 3. We shift the cantilever-tip at a speed of 2.1 nm/s and compress the nanocapsule along the direction indicated by the bigger arrow in Figs. 2(b). The force in-creases from 0 to 4.5 ± 0.5 nN (Figs. 2(b) and 3(b)), and the nanocapsule is compressed by 0.14 ± 0.05 nm, corresponding to a strain of 0.06. During the compression in Fig. 2(b), the cantilever-tip is dented at the interface with the nano-capsule, showing that the nanocapsule is harder than the gold surface. The force increases up to 5.5 ± 0.5 nN, at which point the cantilever-tip is retracted along the direc-tion indicated by the bigger arrow in Fig. 2(c). During re-traction, the cantilever-tip pulls carbon atoms in the outer-most wall and adheres to the nanocapsule, as indicated by the two smaller arrows in Fig. 2(c). Finally, the cantile-ver-tip completely separates from the nanocapsule at a force of 4.9 ± 0.5 nN, as shown in Figs. 2(d) and 3(d).

The compressive force is proportional to the displace-ment from 0 to 5.5 nN as shown in Fig. 3; the nanocapsule elastically deforms in this region. We estimate the spring constant of the present nanocapsule to be 38 ± 17 N/m.

4. Conclusions

We investigated the compressive deformation of individual multi-walled carbon capsules of a few nanometers in di-ameter by in situ transmission electron microscopy with simultaneous force measurement. The carbon nanocapsule of 2.50 ± 0.05 nm diameter was selected and compressed by 6% at a force up to 4.5 ± 0.5 nN. The spring constant of the nanocapsule was estimated to be 38 ± 17 N/m.

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