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Carbon nanocapsules were manipulated inside a high-resolution transmission electron microscope and assembled into single-nanocapsule junctions sandwiching between two gold electrodes. The electric conductivity was measured simultaneously with the lattice imaging of structural dynamics. It was found that the differential conductance of the junction at bias voltages from 0 to 0.20 V corresponded to half of quantized conductances, i.e., $0.5G_0$ where $G_0=2e^2/h$ is the conductance quantum, e is the electron charge, and h is Planck's constant. At bias voltages larger than 0.20 V, the interface structure between the capsule and the electrode changed and the differential conductance increased to $1G_0$. The study showed that carbon nanocapsule junctions are quantized conductors.

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Single molecule junctions are the smallest possible structures of advanced electronic devices, typically consisting of two electrodes sandwiching a single molecule.[1–3] For single fullerene C_{60} molecule junctions, the electric transport has been studied both theoretically and experimentally.[4–12] However, one anomaly has been a common obstacle to the progress in this field of study; the measured conductances across single C_{60} molecules have not been consistent with the calculated conductances, i.e., metallic electron transport. It is pointed out that the conductances through the junctions are affected by interface structures between a C_{60} molecule and two electrodes.[9–12] Therefore, it is more desirable to observe the interfaces while performing the conductance measurements. We have recently developed an experimental method to manipulate two nanometer-sized tips in a transmission electron microscope,[13] and synthesized multiwalled nanometer-sized carbon capsules, a different form of fullerene molecules to the usual C_{60} molecules.[14] In this study, we assembled the nanocapsule into a junction with two gold electrodes inside the microscope and performed the electric conductance measurement for the junction.

We synthesized single crystalline whiskers composed of C_{60} molecules with submicrometer diameters by a liquid-liquid interfacial precipitation method using a toluene solution saturated with a fullerene powder of C_{60}-3 mol % $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ and isopropyl alcohol.[15,16] The crystalline C_{60} whiskers were heated in high vacuum at 1173 K for 30 min to transform them into amorphous carbon whiskers. The amorphous whiskers were then dispersed on the tip of a gold plate of 50 μm thickness. The gold plate was mounted on a specimen holder (the plate holder) on a transmission electron microscope equipped with a force and electric conductance measurement system.[17] The nanometer-sized silicon tip of a 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 holder). Both the plate and cantilever holders were inserted into the microscope.[17] The cantilever tip on the cantilever holder was brought into contact with one of the amorphous carbon whiskers on the plate holder inside the microscope. We impressed a current into the whisker at room temperature in a vacuum of 1×10^{-5} Pa, and synthesized multiwalled carbon nanocapsules aggregating on the whisker.[14] We separated the cantilever tip from the whisker on the plate tip and stopped current impression. Subsequently, we picked one of the nanocapsules on the whisker using the cantilever tip and transferred it to the surface of the gold plate tip beside the whisker, as illustrated in Figs. 1(a) and 1(b). The transmission electron microscope was operated at an acceleration voltage of 200 kV. The atomistic structural variation was simultaneously observed by the lattice imaging of transmission electron microscopy using a television system. The lattice images were recorded at a time resolution of 17 ms. The variations in electric conductance were measured by a two-terminal method at room temperature.

Figures 2(a)–2(c) show time-sequential high-resolution images of the junction of a multiwalled carbon nanocapsule during tip manipulation. In Fig. 2(a), the nanocapsule is supported between the two surfaces of gold nanotips A and B.

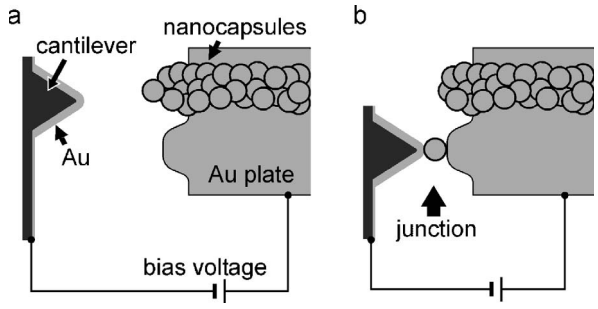

FIG. 1. Illustration of assembly procedure of carbon nanocapsule junction. (a) Picking of nanocapsule on whisker using cantilever tip. (b) Transfer of nanocapsule to surface of gold plate tip beside the whisker.

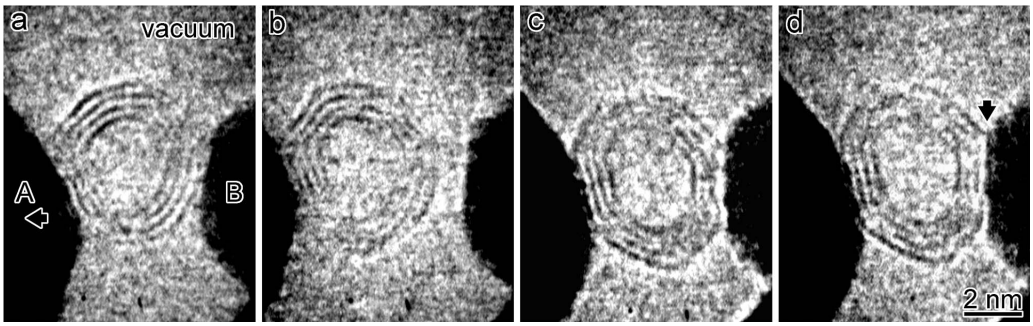

FIG. 2. [(a)–(c)] Time-sequential series of high-resolution images of multiwalled carbon nanocapsule junction at a cycle of contact and separation. The dark regions at the left-hand and right-hand sides show gold nanotips (A and B). The bright regions are vacuums. Time is 0 (a), 0.98 (b), and 30.97 s (c). We started to measure a current-voltage curve at the state observed in (c). During the measurement, bias voltage was increased and the structure of the junction changed to the state in (d). The increase in the interface area is observed in (d) as indicated by an arrow. The differential conductance was $0.5G_0$ and $1G_0$ at the states observed in (c) and (d), respectively. See also Fig. 3.

The outer diameter of the nanocapsule is 5.3 nm, and the capsule is constructed of four graphene shells. The spacing between two shells is 0.3 nm, equivalent to the interlayer spacing of graphite. When tip A is retracted along the direction indicated by the arrow in Fig. 2(a), the nanocapsule is separated from tip B, as shown in Fig. 2(b). Subsequently, tip A is returned to bring the nanocapsule into contact with tip B again, corresponding to one cycle of a mechanically working relay. After contact, the nanocapsule first rotated intermittently between the two tips. Owing to structural change of the interfaces during rotation, the conductance of the junction also fluctuated. After several cycles of contact and separation, the rotation of the nanocapsule was not observed, and its orientation was fixed tightly at larger interfaces with the tips, as shown in Fig. 2(c). The image of the nanocapsule changed from the circle observed in Fig. 2(a) to the ellipse observed in Fig. 2(c) due to rotation. The three dimensional shape of the nanocapsule in Fig. 2 is an ellipsoid with 5.3 nm width along the short axis and 6.1 nm width along the long axis. We selected this stable structure observed in Fig. 2(c) for conductance analysis.

Figure 3 shows a current-voltage curve for the nanocapsule. We started to apply bias voltage at the state observed in Fig. 2(c). The current increases linearly from 0 to 0.20 V, and no gap is observed in current around 0 V. The differential conductance in this region is estimated to be $0.5G_0$, where $G_0=2e^2/h$ is the conductance quantum (e is the electron charge and h is Planck's constant). At a bias voltage larger than 0.20 V, e.g., 0.35 V, the differential conductance increases to $1G_0$. Owing to this increase in bias voltage, the structure of the junction changed as shown in Fig. 2(d); the contact area at the interface between the nanocapsule and the nanotip increases, as indicated by the arrow in Fig. 2(d). We assumed that the contact area is circular and estimated it. The contact area increases from 6.9 nm^2 [Fig. 2(c)] to 9.0 nm^2 [Fig. 2(d)]. The lattice matching at the interface observed at the right-hand side in Fig. 2(d) also increases. It is inferred that such structural changes of the interface were caused by the increase in electrostatic force due to tip approach, and resulted in the increase in the differential conductance.

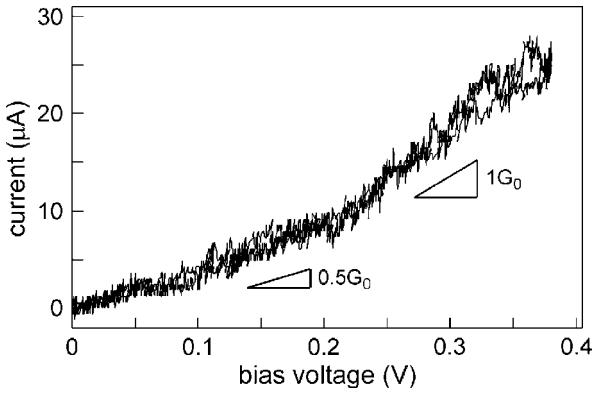

FIG. 3. Current-voltage curve for carbon nanocapsule junction observed in Figs. 2(c) and 2(d).

According to the formula of Büttiker *et al.*,[18] the conductance with N channels is given by $G=G_0\Sigma_{n=1}^{N}\tau_n$, where τ_n is the transmission probability of the nth channel ($0<\tau_n<1$). In this study, the sum of the τ_n for the nanocapsule junction corresponds to 0.5 and 1.0. Theoretical studies show that conductances through Au-C_{60}-Au and Au-C_{20}-Au junctions are 0.55–1.13 and $0.83-1.57G_0$, respectively.[11,12,19,20] The transmission probability of these junctions is reported to be lower than 0.873: 0.110, 0.133, and 0.873 for the Au-C_{60}-Au junctions,[19] and 0.47, 0.47, 0.35, and 0.20 for the Au-C_{20}-Au junctions.[20] These results of the calculation suggest that the transmission probability of the present junction is also lower than unity.

The electron transport with the regular quantized conductance has been observed in metal-element nanocontacts.[21] It was reported that the band gap of fullerenes consisting of more than 70 carbon atoms becomes smaller than that of the C_{60} molecules owing to the increase in the number of carbon atoms.[22–24] The number of constituent carbon atoms of the present nanocapsule observed in Fig. 2 is larger than 70. The increase in the atom number may contribute to no gap-like conductance of this carbon nanocapsule junction at lower bias voltages around 0 V, as observed in Fig. 3.

In conclusion, we investigated the electron transport

through a single carbon nanocapsule supported between two gold electrodes. Current-voltage curves were measured simultaneously with the observation of the interface structures between the nanocapsule and the electrodes. It was found that the carbon nanocapsules showed quantized conductance and can be utilized for various components for carbon device technologies.

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