Controlling Atomic Joints between Carbon Nanotubes by Electric Current

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Using a transmission electron microscope and a nanomanipulator, we explored the early head-to-head coalescence of two capped carbon nanotubes (CNTs) under induction of electric current. We measured detaching forces for coalesced CNTs, showing discrete identifiable values attributable to van der Waals interaction, single sp^2-like bonds, and double sp^3-like bonds by comparing them with forces obtained using molecular dynamics simulations. Our results underscore the feasibility of atomically controlled junctions of CNTs tuned by the amount of the electrical current.

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The properties of nanodevices are largely dependent upon atomic configurations at connections among nanomaterials, electrodes, and substrates as well as the electronic states of the respective nanomaterials themselves [1–4]. Because of the low dimensionality of the nanomaterials and the imperfection of the connection, the electronic structure of the whole device is affected sensitively by the local atomic structure at the connection. For CNT device applications, it is necessary to determine the atomic structures and control those structures' formations precisely. For instance, the connection between CNTs with different chirality is known to show a function such as rectification [2,3]. Nanodevices using quantum dots are also an interesting device application of junction structures with CNTs [4]. Furthermore, the connections among nanotubes might correspond to connections between main units of devices and electrodes because CNTs are also anticipated for use as electrodes.

Recently, pioneering works on intended junction formations in experiments have been done using transmission electron microscopes (TEMs) equipped with a manipulator [5,6]. In those experiments, the junctions were formed via the head-to-head coalescence of two capped CNTs. Theoretical studies have also been performed for coalescence of two capped CNTs at the tips [7,8]. They explore the possibility of a Stone-Wales transformation intensively to explain the structural deformation and formation of CNT junctions. For the initial atomic connection, they merely expect the formation of sp^2-like bonds because other connections by sp^3-like bonds are unstable or energetically unfavorable. However, the correspondence between simulations and experiments remains unclear; moreover, it is difficult to clarify the atomic processes for coalescence of CNTs in experiments. Consequently, it is important to study the atomic processes of coalescence through formation of initial contact to the development of a sp^2 network because those are interesting in nanoscale science and are expected to be informative for the controlled and systematic construction of nanodevices.

Our group has been working intensively on construction processes for nanodevices such as cutting [9,10], curing topological defects [11], formation of plastic bends [12,13], and elongation [14]. As described in this Letter, we specifically examine the initial stage of the coalescence of CNTs and identify the atomic structures at the contact by comparing the measured forces for detachment with those obtained through molecular dynamics simulations. The measured detaching forces between coalesced CNTs show discrete values that can be assigned to a particular atomic structure by performing molecular dynamics simulations. Furthermore, the values were found to depend on the electric current-induced through the coalescence of the two CNTs. Hereinafter, we call this current "current for coalescence (CFC)." The results presented herein strongly suggest that atomic bonds and the atomic configuration of the contact can be controlled using the applied CFC.

To explore the initial connections formed between two capped CNTs, we used TEM and a nanomanipulator. The CNTs, purchased from Nanocyl S. A., were aligned and protruded from the edge of the Si substrate, which had been coated with Pt to produce a conductive surface of a so-called CNT cartridge [15]. The CNT cartridge was set on a manipulation stage installed in a TEM. A Pt-coated Si cantilever for a scanning probe microscope was set on the other stage, which was adjustable using a piezoactuator.

We first prepared two capped CNTs protruded from multiwalled CNTs by cutting a single CNT using an excess-current-induced process. The Pt-coated Si tip approached the end of an individually aligned CNT; a voltage was applied between the cartridge and the Si tip to pass current through a CNT, as presented in Fig. 1(a). Figure 1(e) depicts a TEM image of a typical bridged CNT. Most CNTs examined were multiwalled CNTs with three or four layers and were less than 20 nm long. Application of excess current of ca. 2.2 μA/nm (circumferential current density) [12] sublimated the layers from the outer to inner layer-by-layer at the middle of the bridged CNT. Finally, the innermost tube was cut. Both cut CNT tips were capped. Their diameters were less than or around 1 nm, as presented in Fig. 1(f).

Both tips of the CNTs were manipulated to contact each other [Fig. 1(g)]. Because of the van der Waals (vdW) force, the tips were mutually attracted spontaneously when they were close; no additional pressure was applied after they contacted. Then, CFC was passed through the contact point to generate C-C bond formation there. The CFC was increased gradually to reach a target value (0.1, 0.3, 0.5, 1.0 μA); then it was maintained for 30 s to ensure the current treatment.

To measure the contact force, the Si cantilever was pulled by the piezoactuator after CFC treatment. The Si cantilever was bent by the contact force [Fig. 1(d)]. The contact was broken when the cantilever was bent by δx, which was measured as the difference in the voltage applied to the piezoactuator, corresponding to the force to break the bonds between the two CNTs. The force was calculated from the bending (δx) using the spring constant, 0.03 N/m, of the Si cantilever. Here, the accuracy of the measured force is within ±0.1 nN, as estimated from the resolution of TEM measurement and the spring constant of the cantilever [16]. We also confirmed that no interlayer sliding occurred in this measurement.

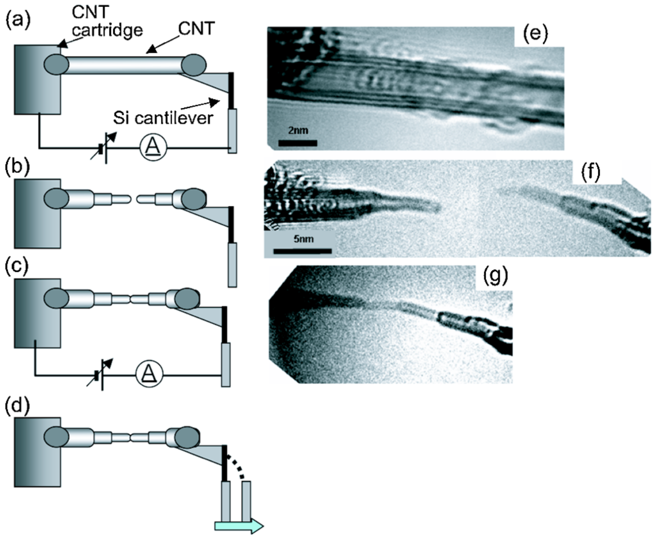

FIG. 1 (color online). (a)–(d) Schematic illustrations and (e)–(g) TEM images showing measurement of the contact force between two capped CNTs. (a),(e) A CNT is bridged between the cartridge and Si tip. (b),(f) Two capped CNTs protruding from multiwalled CNTs are prepared using a current-induced cutting of a single CNT. (c),(g) The two capped CNTs are mutually contacted; then current for coalescence (CFC) is applied. (d) To measure the bonding force, the Si cantilever is moved away. The bonding force bends the Si cantilever. The contact is broken when the cantilever is bent by δx. This δx and the spring constant of the cantilever provide the bonding force between the CNTs.

Figure 2 portrays the contact force, which is shown as a function of the current for 14 measurements. It is readily apparent that we can classify the values of measured forces into three discrete groups. Data belonging to Group I were measured using CFC less than 0.5 μA and show the contact forces as less than 2.1 nN with an average value of 1.5 nN. Some data measured using CFC of 0.5 μA and 1.0 μA are classified into Group II, which has an average force of 11.2 nN. The highest force belonging to Group III in the measurement is 21.0 nN, which was obtained with CFC of 1.0 μA. Fortunately, clear gaps exist in measured forces among the groups we divided, which is the same order of the variation 5 nN. Therefore, it is natural to divide the measured data into several groups. We estimated that each group corresponds to a specific atomic configuration with only a few chemical bonds between nanotube tips by comparing those values to those of carbon–carbon covalent bonds.

Group I includes data obtained with CFC 0 μA. Consequently, the measured force might be attributable to a noncovalent bond. We can estimate the vdW force acting between the two capped CNTs using a simple model of two spheres with diameters of D_1 and D_2 placed with a gap of d. This model gives the vdW force as

$$F = -\frac{\partial}{\partial d}\frac{AD_1D_2}{12d(D_1 + D_2)} = \frac{AD_1D_2}{12d^2(D_1 + D_2)}. \qquad (1)$$

Applying reasonable parameters of $D_1 = D_2 = 1$ nm, $d = 0.34$ nm and the Hamaker constant of $A = 6 \times 10^{-19}$ J [10] to Eq. (1), we have 0.43 nN. This rough estimation is consistent with experimental results. Meanwhile, one can expect that Groups II and III are associated with some covalent bonds.

To clarify the atomic scale origin of measured forces in Group II and III as well as atomic arrangements throughout connections and disconnection between the tips of CNTs,

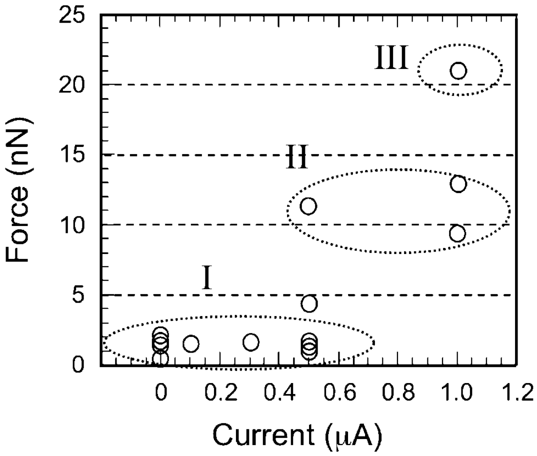

FIG. 2. Contact force between the two capped CNTs, shown as a function of current for coalescence. The current is designated as CFC in the main text.

we performed constant temperature tight-binding molecular dynamics simulations [17,18]. Herein, we demonstrate that a small model consisting of two C_{60}s is sufficient to reproduce discretized forces, which suggests that forces are determined by local covalent bonds. We use the parameterization of atomic interaction by Xu [17] *et al.*, which is known to reproduce the properties of covalent bonds of carbon accurately, such as those of graphene, diamond, and other carbon clusters. Although we did not include the vdW-like weak interaction between nanotube tips throughout the molecular dynamics, the forces to break covalent bonds are much larger than such weak interactions. For that reason, we neglected them.

We modeled the connections between tips of CNTs as one or two bonds formed between two C_{60} fullerenes, as depicted in Figs. 3(a)–3(d). To simulate the experimental procedure, two fullerenes were detached by pulling the carbon atoms at the edges indicated by the red spheres in Fig. 3 along the lateral axis under a constant temperature [19]. The tensile force is given by the sum of the force acting on the constrained carbon atoms of one side. As described in this Letter, we define the tensile force as the average of two tensile forces in opposite directions. We used the constant velocity of 0.1 nm/ps for the constrained carbon atoms at each end.

When an additional velocity for constrained atoms (a load rate) is much lower than those of atomic vibrations at the connections, the potential barrier for the bond breaking is governed by the thermal effect: the higher temperature lowers the potential barrier. The thermal fluctuation further lowers the potential barrier. The condition corresponds in usual experiments. However, for a higher load rate comparable to those of atomic vibrations, the fluctuation is no longer governed merely by the temperature and can artificially increase the tensile force in the simulations. Although our theoretical tensile velocity, which was introduced to reduce the computational time, is higher than those of experiments, we confirmed that the tensile velocity remains lower than atomic vibration; it is sufficient to avoid the artificial effects. When the velocity was decreased to 0.033 nm/ps, the change in the tensile force to break the connection was within the error of thermal fluctuation as 1–5 nN at 300 K.

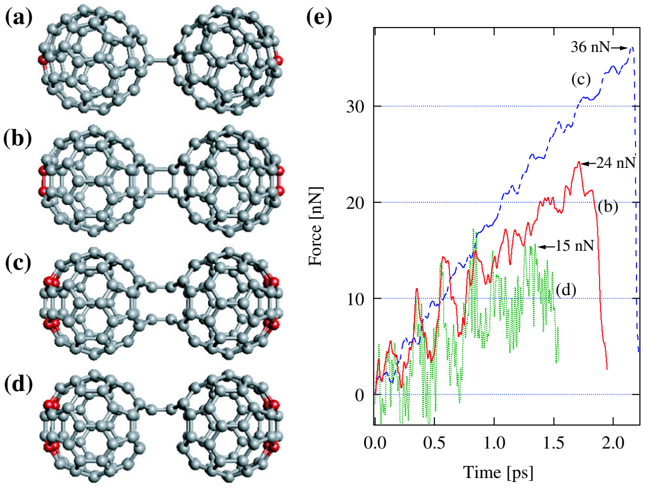

FIG. 3 (color online). Bonding structures between C_{60} molecules with (a) one sp^3-like bond, (b) two sp^3-like bonds, (c) two sp^2-like bonds, and (d) one sp^2-like bond mimic the connections between nanotube tips. (e) The tensile force to break the connection is a function of the simulation time.

The bonding structure depicted in Fig. 3(a) consists of only one sp^3-like bond, where two fourfold carbon atoms connect the fullerenes. This structure, which was stable only under doping of more than two electrons per system [20], is realized at the nanotube tips. The tensile force for detachment was ca. 4 nN at 0 K, which resembles the value of thermal fluctuation.

Here, the binding potentials for the covalent bonds are rather short range compared to the weak noncovalent bonding such as vdW interaction. The local atomic vibration can therefore break the bond rather easily because the kinetic energy of atoms frequently goes beyond the corresponding value of room temperature, especially at the contact. Furthermore, there are reaction barriers not only for the bond breaking but also for bond formation with the atomic configurations used in our simulations. The formations of the bonds are always endothermic. Consequently, once the bond is broken, it is difficult to make connections again. Actually, the connection between fullerenes with a single sp^3-like bond is easily broken at room temperature in our simulation.

On the other hand, the binding potential for the weak noncovalent bonding is rather long range. Therefore, the fluctuation of the vibration of the individual atom does not affect the global connection at room temperature. Consequently, one can observe the tensile force for breaking the bond in Group I, which is smaller than the thermal fluctuation of the force at room temperature. We conclude that the single sp^3-like bond would be difficult to maintain within our experimental setup at room temperature.

The robustness of the interconnection is completely different for two sp^3-like bonds between C_{60}s, where four fourfold carbon atoms form a four-membered ring at their connection [Fig. 3(b)], which is known as a structure for the C_{60} dimer. The tensile force used to break the connection as a function of simulation time is presented in Fig. 3(e). The force is about 24 nN, which corresponds to the tensile forces of group III.

To clarify the effect of lattice mismatch at the tips of two CNTs, we further performed the tensile breakdown with different initial torsional angle. When the initial torsional angle was varied from 0–3° by twisting the edge-constrained carbon atoms for the connection with two sp^3-like bonds, the tensile force was lowered only by ca. 5 nN (Fig. 4) because the overall atomic rearrangements reduce the internal strain acting on the connection. The tensile force for breakdown was kept constant under a small lattice mismatch.

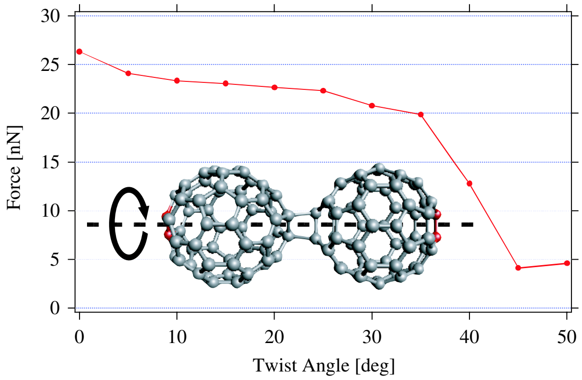

FIG. 4 (color online). The tensile force which breaks the connection is a function of the torsional angle along the axis through the center of the two fullerenes.

The connection formed by two sp^2-like threefold carbon atoms between C_{60}s [Fig. 3(c)] was more robust than that of the sp^3-like bond connection; the corresponding tensile force was about 36 nN [see Fig. 3(e)]. Because the interaction between the pair of sp^2-like bonds was sufficiently small, the tensile force for a single sp^2-like bond [see Fig. 3(d)] was about half of it, i.e., ca. 15 nN, as portrayed in Fig. 3(e). The value corresponds to the group II tensile strengths in our experiment.

In our experiments, we apply current of more than 1.0 μA to study the further development of the intertube connection. However, no difference appeared after applying just over a 1.0 μA current. With more than 10 μA current, the image at the CNT tips begins to change gradually; finally, the nanotubes coalesced at the tips over the current of 15 μA. Therefore, there must be very high-energy barriers for the coalescence of nanotubes at the tips compared to that of the formation of initial atomic connections. When applying high currents of 15 μA, the further development of the coalescence needs no more rise of currents. We did not observe two sp^2-like bonds in our experiments. Therefore, the two sp^2-like bonds might be formed only at the beginning of the coalescence reaction.

The load-rate dependence of the tensile strength for the molecular recognition is studied quite intensely recently in AFM measurements of organic molecules [21], where the important chemical bonds are rather weak noncovalent bonds. However, we did not observe the load-rate dependence of the tensile strength for load rates of 1–5 nm/s in our experiments because the load-rate dependence would appear in the reaction involving many atoms and/or complex systems, as organic molecules with higher-order structures have appeared.

In conclusion, covalent bonds are generated with a head-to-head contact of two capped CNTs when a CFC of 0.5 μA or more is applied. Results show that the formation of two sp^3-like bonds is a favorable atomic configuration at a very early stage of the head-to-head coalescence of two capped CNTs; although the atomic configuration with two sp^2-like bonds was not observed in our experiments. Consequently, we expect that the formation of two sp^2-like bonds requires higher energy than those of two sp^3-like bonds; then, more covalent bond networks are immediately developed at such high-energy conditions, probably after formation of two sp^2-like bonds. To understand the mechanism of this coalescence deeply, it is important to observe the route from the initial covalent bond formation described here to the neck (thin intermediate tube) formation. This remains as a subject for additional study.

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[20] We confirmed that the single sp^3-like bond connection between the C_{60}s is stable under electron doping using density functional method within local density approximation. The structure is a metastable structure; such a doping condition would be realized easily under the condition with current induction in experiments.
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