# Stability of Carbon Nanotubes: How Small Can They Be?

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Experimental evidence has been found for the existence of small single wall carbon nanotubes with diameters of 0.5 and 0.33 nm by high resolution transmission electron microscopy, and their mechanical stability was investigated using tight-binding molecular dynamics simulations. It is shown that, while the carbon tubes with diameters smaller than 0.4 nm are energetically less favorable than a graphene sheet, some of them are indeed mechanically stable at temperatures as high as 1100 °C. The 0.33 nm carbon tube observed is likely a $(4, 0)$ tube and is indeed part of a compound nanotube system that forms perhaps the smallest metal-semiconductor-metal tubular junction yet synthesized.

Sun *et al.* [1] reported that carbon nanotubes with diameters as small as 0.5 nm can be synthesized, showing a high resolution transmission electron microscopy (HRTEM) image of such a tube closed at one end by half of a $C_{36}$ cage. This discovery broke the eight year record held by 0.7 nm nanotubes [2] whose diameter matches that of the $C_{60}$ bucky ball. In this Letter, we report our finding of a 0.33 nm carbon nanotube that was grown from a larger nanotube inside an electron microscope. Although this small nanotube is energetically less favorable than a graphene sheet [3], we show using tight-binding (TB) molecular dynamics (MD) simulations that it is indeed mechanically stable at temperatures as high as 1100 °C. We propose that this very small nanotube is nucleated from a defective graphene sheet from which two neighboring carbon atoms have been knocked out or displaced, the resultant growth being kinetically driven. The compound nanotube system we observed is likely to be a $(11, 11)$-$(4, 0)$-$(11, 11)$ T junction, which forms perhaps the smallest metal-semiconductor-metal tubular junction yet synthesized. A novel feature of this small nanotube is that it can, in principle, be grown on nanotubes of any helicity. This offers the exciting prospect of forming junctions among tubes with different electrical properties which could have implications for the design of future nanoelectronics devices.

The thermodynamic stability of carbon nanotubes is determined by a competition between the increase in energy due to the bond-bending strain introduced by rolling the planar graphene sheet into a tube and the decrease in energy due to the dangling bonds on the edges of the graphene sheet bonding together on the formation of the tube. Since the strain energy is expected within continuum elasticity theory to vary inversely with the square of the tube diameter [4], sufficiently small tubes will become thermodynamically unstable, a simple Tersoff-like atomic potential [5] predicting a critical tube diameter of

0.4 nm [3]. This is illustrated in Fig. 1a where the energy of unrelaxed carbon nanotubes with different diameters is compared to that of the corresponding graphene sheet, the bonding energies being calculated using the tight-binding parametrization of carbon by Xu *et al.* [6] within the local-charge-neutrality approximation [7]. As is customary, the carbon nanotubes have been characterized by their chiral vectors $\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2 = (n, m)$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit cell vectors of the graphene sheet [8]. Assuming that the C—C bond length in graphene is 1.42 Å, the six smallest nanotubes $(2, 0)$, $(2, 1)$, $(3, 0)$, $(2, 2)$, $(3, 1)$, and $(4, 0)$ will have unrelaxed diameters of 1.566, 2.071, 2.349, 2.712, 2.823, and 3.132 Å, respectively. We see from Fig. 1a that all the carbon nanotubes with diameters greater than 0.4 nm are energetically more favorable than the corresponding graphene sheet, in good agreement with the earlier Tersoff-potential predictions of Sawada and Hamada [3]. We should note, however, that there can be sizable discrepancies of more than 30% between the predicted Tersoff and TB values for the smallest tube diameters due to the explicit neglect of the $\pi$ bond within the Tersoff formalism [5].

The mechanical stability of the carbon nanotubes was investigated by running TB molecular dynamics simulations. We see from Fig. 1b that the smallest nanotube, $(2, 0)$, is unstable even at temperatures as low as 1 K. The geometrically constructed $(2, 0)$ tube, which is illustrated in Fig. 1a, relaxes rapidly to a lower energy structure which is basically the same as the original structure but with different bond lengths and bond angles. However, after about 300 fs this structure changes gradually into a two-dimensional layer structure that leads eventually to a graphene lattice. The next smallest tube, $(2, 1)$, is metastable at 1 K but becomes unstable by room temperature with the mechanical instability moving in from the two ends of the tube as bonds are broken. The achiral $(3, 0)$ nanotube, on the other hand, is mechanically stable
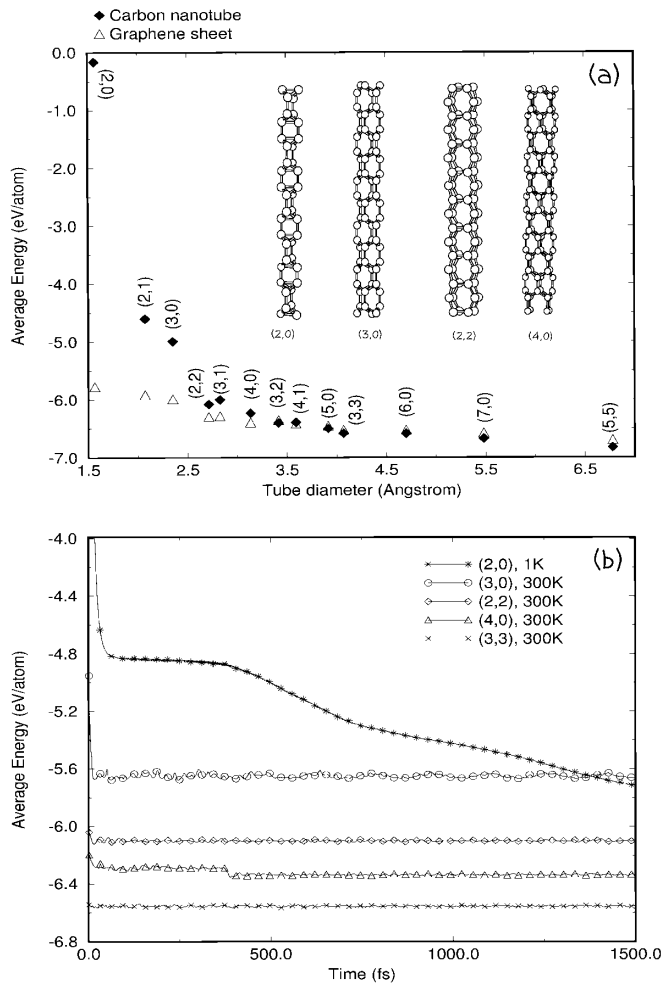
FIG. 1.   (a) Comparison of the average total energy per atom for SWCNTs with that of the corresponding graphene sheets for tube diameters less than 0.7 nm. (b) MD simulated average energy per atom as a function of time for five achiral nanotubes. The time step is 1.0 fs, which is $1.0^{-15}$ s.

at room temperature, with the time average of the total energy remaining constant over the 1500 fs shown in Fig. 1b. We found that all the other nanotubes with diameters larger than that for $(3, 0)$ were mechanically stable at room temperature, although the $(4, 0)$ tube displays a small energy step at about 370 fs in Fig. 1b. This corresponds to the four standing carbon atoms in Fig. 1a bonding together to form a cap that comprises one square at the top, surrounded by four pentagons. Once formed, the cap remains stable with the energy lowered by about 5 eV. All the nanotubes with diameters greater than or equal to $(4, 0)$ are found to be mechanically stable at 1100 °C when experimentally it is known that vapor phase growth occurs.

Our experimental single wall carbon nanotubes (SWCNTs) were produced from clothlike soot, which was prepared by the dc arc-discharge method [9]. The raw soot was then purified and most of the so-obtained SWCNTs were determined by combined high resolution TEM and Raman spectroscopy to be of the $(n, n)$ type, with $n$ ranges

from 8 to 11 [10]. In this study, HRTEM observations were performed using a field-emission gun transmission electron microscope (Philips CM200/FEG), equipped with a GATAN imaging filter. Figure 2 is a HRTEM image showing some graphite crystallites and two SWCNTs. Fringes resulting from the graphite crystallites correspond to a lattice spacing of 0.34 nm, and these fringes were used for calibrating the diameters of the carbon nanotubes. The bigger tube to the bottom left of the figure shrinks toward its end, but its diameter is of the order of 1.55 nm, and corresponds roughly to a $(11, 11)$ tube. The smaller tube to the bottom right is an as-grown tube, with a diameter of 0.5 nm. This tube is of the same type as found by Sun *et al.* [1], and may be regarded as originating from a $C_{36}$ molecule. Unlike the tube reported in [1], which is embedded in the innermost shell of a multiwall carbon nanotube, Fig. 2 shows that the small tube is a SWCNT and the tube is clearly visible. Our experiments show that this tube remains stable at room temperature under the electron beam, and that this tube existed in the sample prior to our TEM observations.

Figure 3 shows two HRTEM images taken in a period of about one minute. These HRTEM images were taken from the same sample and with the same magnification as that of Fig. 2. Figure 3a shows that two SWCNTs intersect at a junction to the left of the figure. The two SWCNTs were found to have a diameter of about 1.55 nm, which corresponds to a $(11, 11)$ tube and are metallic according to the rule that a nanotube is metallic if $(2n + m)$ is a multiple
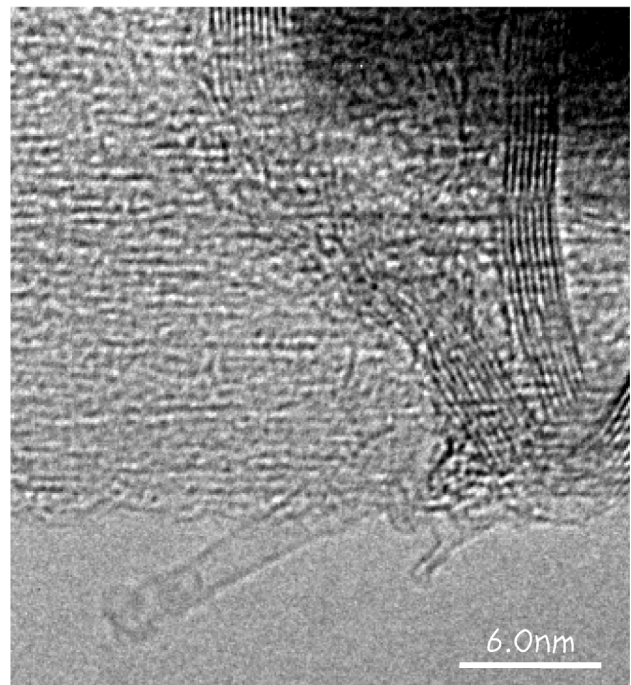


FIG. 2.   High resolution TEM image showing graphite sheets to the top right of the figure, and two SWCNTs to the lower half of the figure. The larger tube has a diameter of the order of 1.5 nm, and the smaller tube has a diameter of about 0.5 nm.
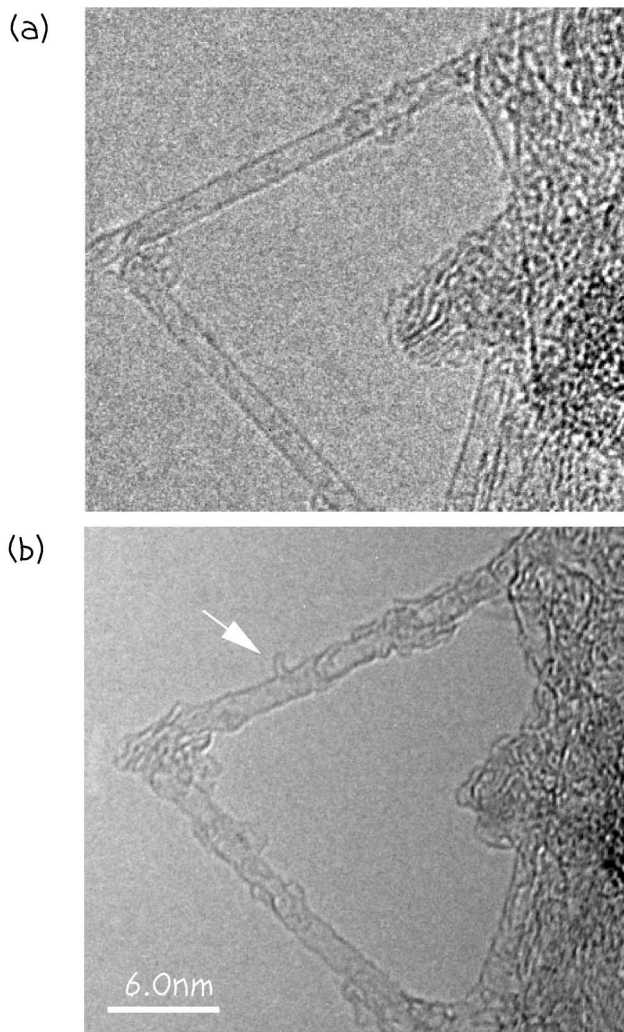
(a)

(b)



FIG. 3.　High resolution TEM images show (a) two intersecting SWCNTs with a diameter of 1.5 nm, and (b) formation of a 0.33 nm SWCNT.

the next achiral tube is $(5, 0)$ having an unrelaxed diameter of 0.4 nm.

We have shown earlier that a tube with a diameter less than 0.4 nm is energetically less favorable than a graphene sheet [3]. A carbon tube with a diameter as small as 0.33 nm is therefore unlikely to have been formed from a graphene sheet. In Fig. 4, we propose a two-step model for the formation of the $(4, 0)$ tube. In the first step, either two carbon atoms are removed from an otherwise perfect graphene lattice (knocked off by incident electrons) or displaced from the graphene sheet following the breaking of two bonds (via excitation of electrons and consequent weakening of the carbon bonds when the corresponding antibonding states are occupied by these excited electrons). The first situation leads to the formation of four dangling bonds, and, subsequently, four carbon atoms are attracted
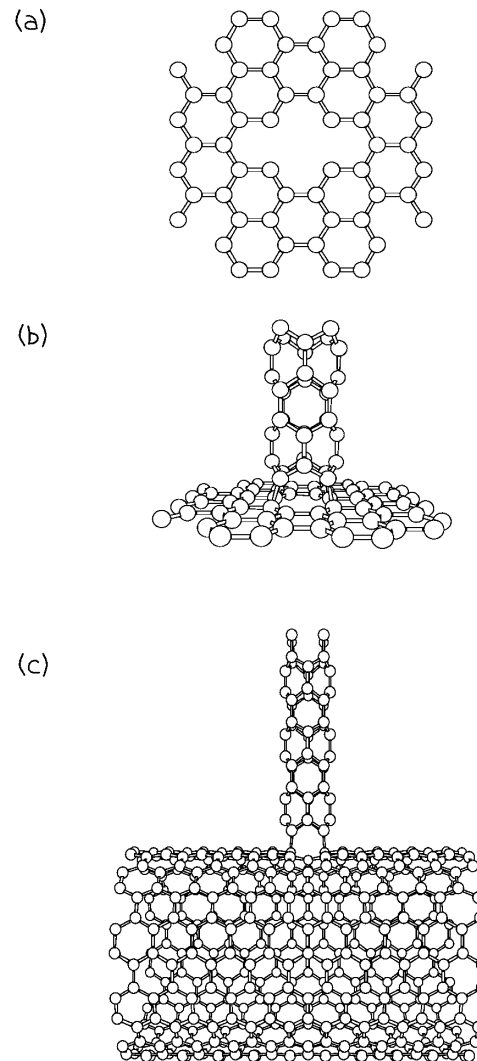
(a)

(b)

(c)



FIG. 4.　Atomic models showing (a) formation of four dangling bonds via taking away two carbon atoms from a graphene sheet, (b) formation of a $(4, 0)$ tube and graphene sheet junction, and (c) formation of a T junction $(11, \overline{1}1)$-$(4, 0)$-$(11, \overline{1}1)$.

of 3 [11]. In all other cases, the nanotubes are expected to be semiconducting with an energy gap of the order of 0.5 eV [11–13]. Under the electron beam irradiation for about ten seconds, a tiny object with cylindrical symmetry (which was verified by tilting experiments) is found to have grown from the parent tube (marked by an arrow in Fig. 3b). Closer examination of the image contrast of this cylindrical object reveals that it is hollow, showing the same contrast as that of a small tube. Figure 3b shows that this tiny tube has been connected nicely to its parent tube without introducing much lattice distortion, suggesting that the tube must be a tube of high symmetry. Direct measurements of the image contrast suggest that the tube diameter is about 0.35 nm. But this procedure is known to be not very accurate, and image simulations reveal that this apparent diameter is slightly larger than the real diameter of the tube. The closest match to this tubular object is the relaxed $(4, 0)$ tube with a diameter of 0.33 nm, while

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to these four dangling bonds, followed by more carbon atoms stacking on top of these atoms to form a $(4,0)$ tube. In the second situation, only two bonds are broken, and the two relevant carbon atoms may move away from the graphene sheet which, subsequently, may incorporate a carbon dimer and form the first four atom ring of the $(4,0)$ tube. In both cases, the growth is kinetically driven. In principle, similar damage to a graphene lattice may be achieved via a more controlled way using a scanning tunneling microscopy tip and also by using other radiations, such as a laser beam. Our MD simulations suggest that the growth of the $(4,0)$ tubes is possible at temperatures as high as 1100 °C, but not much higher. This is because at higher temperatures, such as at 3400 °C, the $(4,0)$ tube is not mechanically stable and will transform into graphene-like structure. At not exceedingly high temperatures, the compound structure composed of the tube and graphene sheet is very stable.

One novel feature about the structure shown in Fig. 4b is that the graphene sheet to which the $(4,0)$ tube is joined may be rolled up to form another nanotube of practically any type. It can be either a $(11,11)$ tube, as shown in Fig. 4c, or a zigzag $(11,0)$ tube. This means that a small $(4,0)$ tube may be connected equally well to an armchair tube which is known to be metallic in nature, and to a zigzag tube which may sometimes be semiconducting with a nonzero energy gap. In fact, the small $(4,0)$ tube may connect two tubes of different helicities together and therefore serve as a nanojunction with desired properties. Our experimental findings therefore point to a new way to form junctions among tubes with different characteristics, and our MD simulations suggest that these structures are mechanically stable.

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