Growth Energetics of Carbon Nanotubes

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The growth energetics of carbon nanotubes during arc discharge conditions are investigated. *Ab initio* molecular dynamics calculations show that the electric field alone cannot stabilize the growth of open metallic tubes. The addition of atoms and small clusters to tubes were studied using realistic atomic potentials. Deposition on tubes narrower than ~3 nm leads to nucleation of curved defects (adjacent pentagon pairs) and eventual tube closure, while deposition on wider tubes favors the formation of hexagons and isolated pentagons, thereby promoting open-ended growth.

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The recent discovery of graphitic nanotubes in an arc discharge [1–3] has aroused much interest in the scientific community, due to their unusual structure and electronic properties. Experimental and theoretical studies show that nanotubes are potential candidates for wires of very high tensile strength and that they exhibit interesting material characteristics as composites, catalysts, molecular straws, and switches [4–7]. Recent experiments, utilizing metal catalysts [8] or plasma decomposition of benzene [9], have led to the synthesis of nanotubes ranging from 1 to 200 μm.

In an arc discharge, bundles of nanotubes with diameters ranging from 2 to 20 nm grow at the graphite cathode in an inert gas atmosphere [1–3]. Because they form under highly nonequilibrium conditions, determining their growth mechanisms is a problem of considerable complexity. While it was initially believed that the tubes grow through the addition of atoms to the caps of closed tubes [10], recent experiments show that the growth of these tubes is open ended [3]. This is quite surprising, because the presence of the dangling bonds at the end of an open tube should favor the closed tube geometry. It has been proposed that the high electric field (**E** field) present at the tip of the nanotube is the critical factor that prevents it from closing [11].

In this Letter, we present results of an extensive theoretical study of the growth of carbon nanotubes in an arc discharge. Surprisingly, an unrealistically long critical tube length is required before the **E** field alone can stabilize the growth of open tubes. Examination of the low-energy structures formed upon atomic depositions show that tube closure is seeded by the formation of adjacent pentagon structures. Their formation is energetically favorable only for tubes narrower than a critical diameter, estimated to be ~3 nm. Wider tubes stabilize the formation of all-hexagonal structures, thereby allowing for continued growth. These results shed light on the mechanisms of noncatalytic growth of nanotubes and explain the absence of narrow tubes in the arc discharge growth.

To assess the role of the **E** field, we solved the Laplace equation for the arc discharge geometry as a function of tube radius R and length L. A finite difference program [12] that utilizes a triangular mesh of variable size in a cylindrical geometry was used. For the open tubes, a wall thickness of 1 Å was assumed. Closed tubes were constructed by capping the open tubes with a hemisphere of the appropriate size. In experiments using the arc discharge, a plasma sheath forms next to the cathode. A uniform potential drop equal to the ionization potential for carbon ~10 V occurs over the thickness of the sheath [13]. In our calculations, the nanotubes protruding from the cathode were assumed metallic, in order to present the best case scenario for the **E** field. They were immersed in a uniform field of 0.01 V/Å, corresponding to a plasma sheath of 100 nm [13]. For a closed tube in a uniform field, the only length scales in the problem are L and R. It can be shown by scaling arguments that the **E** field enhancement at the tip E_{tip}/E_0 is a function of only the ratio L/R. A numerical fit to our calculated values for *closed* tubes of various lengths and diameters yields the formula

$$E_{\text{tip}} = E_0\left[0.87\frac{L}{R} + 4.5\right]. \quad (1)$$

The open tube in a uniform field has the wall thickness as an additional length scale besides L and R, and therefore the field-enhancement E_{tip}/E_0 is an explicit function of L and R. Figure 1 shows the computed **E** fields for open tubes of various diameters as functions of the tube length. The numerical data for the *open* tubes is well fit by the formula

$$E_{\text{tip}} = E_0\left[2.35R^{0.65}\frac{L}{R} + 4.55\right], \quad (2)$$

where R is in nm. The above formulas are valid within the range $0.2 < R < 10$ nm, $20 < L < 60$ nm, and an L/R ratio >5. It is clear that for both open and closed tubes of fixed lengths, the **E** field at the tip *decreases* as the width of the tube is increased. Note that even for the narrowest tube, i.e., the buckytube of diameter 0.7 nm, the tube has to grow to a length of $L_{\text{critical}} \sim 30$ nm before E_{tip} becomes ~1 V/Å, the estimated field strength required to influence a strong chemical bond.

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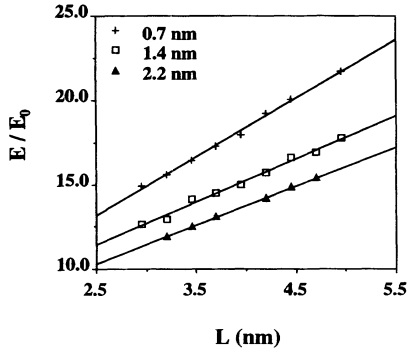

FIG. 1. Electric field enhancement (E/E_0) at the tip of an open metallic tube of various diameters in a uniform background field E_0.

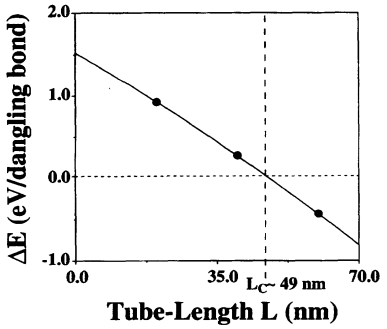

FIG. 2. Energy difference ΔE (per dangling bond) between an open, metallic 0.7 nm tube in an electric field and a closed tube of the same size in zero field, as a function of tube length. The crossover in tube stability occurs at $L_{\text{critical}} \sim 49$ nm.

To obtain a more accurate value of L_{critical}, the effect of the **E** field on the tips of carbon nanotubes was investigated using *ab initio* molecular dynamics [14]. The carbon atoms were represented by a soft core pseudopotential [15] that reproduces the structural properties of diamond and graphite. The effect of the external **E** field was incorporated by an additional external energy term in the local-density functional [16]. Tips of both open and closed tubes with 0.7 nm diameter were constructed. The small tube diameter was chosen in order to maximize the effects of the **E** field and to minimize the computational cost. For the open tube tip, six layers of an armchair tube (known to be metallic [7,17]) were used, while the closed tube tip was constructed by replacing the top three layers of the open tip by a hemispherical cap of C_{60}. The tube tips were about a diameter long, since the differences in induced charge between the open and closed tube tips occur only in this range [18]. A 26 Ry kinetic-energy cutoff was used in the calculations, which corresponds to about 36 000 plane waves. The supercell included a vacuum region 0.7 nm wide in all cartesian directions, so as to effectively isolate the tube tip from its periodic images.

Both tube tips were atomically relaxed in the absence of the **E** field. It was found that the presence of dangling bonds at the open tube tip favors the closed tube structure by 1.6 eV/dangling bond. As the **E** field is turned on, the energy difference between the open and closed tubes decreases slowly. In order to present the best case scenario for the positive role of the **E** field in enhancing open-ended growth, we compare the energy of the open tube in the **E** field to that of the closed tube in zero field [19]. The open tip was fully relaxed in **E** fields characteristic of several different tube lengths (as previously calculated through the finite difference scheme). Figure 2 shows the energy difference per dangling bond between the open tube in the field and the closed tube in zero field, as a function of the tube length. The field at the tube tip increases linearly as a function of the tube length L, thereby increasing the electrostatic energy. The slight curvature of the energy vs length curve for the open tip is due to a small linear polarization of the electron charge density by the field. For the 0.7 nm diameter buckytube, the **E** field energetically favors the open tube geometry only for $L > L_{\text{critical}} \sim 49$ nm, which corresponds to a tip field of ~ 1.7 V/Å. Since E_{tip} for a given L decreases with increasing tube diameter, wider nanotubes will have an even larger L_{critical}. However, thermionic and field emission are expected to occur at field strengths smaller than 1 V/Å [13,20], so that the crossover field is unattainable in practice. One therefore concludes that the **E** field cannot be responsible for keeping the tubes open during growth. This is one of the main results of this Letter.

With the **E** field ruled out, open-ended growth must be due to other conditions in the arc discharge apparatus. The idea that hydrogen atoms temporarily saturate the dangling bonds and keep the tube open is attractive but highly improbable [11], due to the almost complete exclusion of H in the arc discharge experiments [1–3]. The presence of a thermal or concentration gradient of sufficient magnitude at the tube tip can also be ruled out [11]. This naturally leads to a model based on local stability of open-ended structures in the accessible configuration space of the nanotubes.

In order to explore the relative stability of the various adatom structures, total energy calculations were performed using classical three-body interatomic potentials of Tersoff's form [21] with parameters due to Brenner [22]. A number of all-hexagon open tubes of varying diameters and helicities were constructed. Carbon atoms, dimers, and trimers were deposited at various orientations on different parts of the open edges. The resulting structures were relaxed by the conjugate gradients method. The most important structures are the ones that form at a "step edge," where a row of hexagons terminates at the tube tip. For tubes with helicities (n_1, n_2) in the notation of Hamada *et al.* [7], the low-energy structures for dimer and trimer deposits are listed in Tables I and II, respectively. For monomer deposits, the only low-energy structure is an isolated pentagon at a step edge.

TABLE I. Relative energies of low-energy structures formed by dimer addition to tubes of different diameters. All structures are at a step edge unless stated otherwise. Lowest energy structures are schematically drawn in Figs. 3(a) and 3(b). Notation for helicity follows Hamada *et al.* [7]. All energies are quoted relative to the minimum-energy structure.

Diameter	Structure	Energy (eV)
0.7 nm	2 adjacent pentagons (5-5)	0.00
helicity (8,1)	Hexagon	0.53
	Pentagon (away from step edge)	2.04
	Pentagon + dangling bond	2.29
1.5 nm	2 adjacent pentagons (5-5)	0.00
helicity (24,2)	Hexagon	0.19
	Pentagon (away from step edge)	1.79
3.0 nm	Hexagon	0.00
helicity (35,5)	2 adjacent pentagons (5-5)	0.01
6.0 nm	Hexagon	0.00
helicity (62,23)	2 adjacent pentagons (5-5)	0.15
Flat sheet	Hexagon	0.00
helicity (14,6)	2 adjacent pentagons (5-5)	1.35

As seen from Table I, for a dimer deposit there are two competing low-energy structures, a hexagon and a 5-5 pair at a step edge [Figs. 3(a) and 3(b)]. The 5-5 pair stabilizes one more dangling bond than the hexagon, but leads to a highly curved structure with a large strain energy. It is energetically favorable only for narrow, highly curved tubes. The hexagons, which lead to open growth, are energetically favored for less curved, large diameter tubes. Other structures, such as a pentagon forming away from a step edge, or a pentagon and a dangling bond at a step edge, are energetically unfavorable, costing ~2 eV each. Trimers also insert themselves preferably at the edges of steps: 5-5-5, 5-6, and 6-5 [Figs. 3(c)–3(e)] are the lowest energy structures for very narrow tubes, with the 5-5-5 being the most stable energetically. As the tube diameter increases, the 5-5-5 becomes unfavorable due to a large strain energy, and the 5-6 and 6-5 become the lowest energy structures. The formation of heptagons at the step edge is energetically unfavorable, both due to strain energy and the presence of additional dangling bonds (energy cost > 1.7 eV).

TABLE II. Relative energies of low-energy structures formed by trimer addition to tubes of different diameters. All structures are at step edge. Lowest energy structures are schematically drawn in Figs. 3(c)–3(e).

Diameter	Structure	Energy (eV)
0.7 nm	5-5-5 (3 adjacent pentagons)	0.00
helicity (8,1)	5-6 pair	0.50
	6-5 pair	0.61
	Heptagon	1.75
1.5 nm	6-5 pair	0.00
helicity (24,2)	5-6 pair	0.01
	5-5-5 (3 adjacent pentagons)	0.16
3.0 nm	6-5 pair	0.00
helicity (35,5)	5-6 pair	0.05
6.0 nm	6-5 pair	0.00
helicity (62,23)	5-6 pair	0.09
Flat sheet	6-5 pair	0.00
helicity (14,6)	5-6 pair	0.46

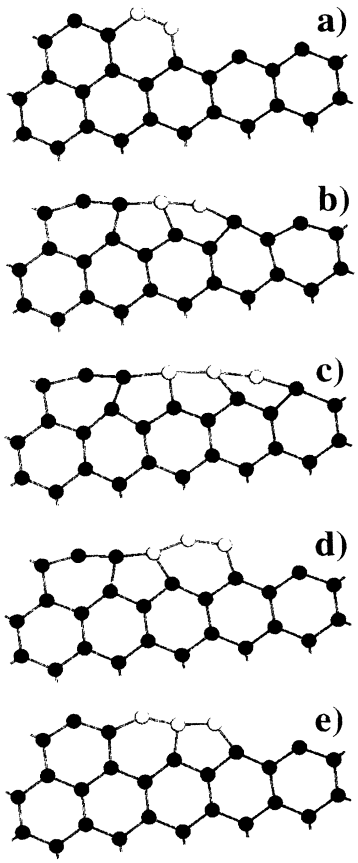

FIG. 3. Low-energy structures formed at the edges of steps: (a) hexagon, (b) 5-5 pair, (c) 5-5-5, (d) 5-6, and (e) 6-5. Structures (a) and (b) result from the deposition of a dimer, while (c), (d), and (e) result from the deposition of a trimer.

The presence of a 5-5 or a 5-5-5 structure at a step edge leads to a highly curved tip that results in tube closure after further depositions. Our calculations thus suggest that narrow tubes cannot grow for long, due to the formation of structures with adjacent pentagons that act as seeds for tube closure. However, tubes wider than ~3 nm stabilize structures with either hexagons or hexagons and isolated (exposed) pentagons at the step edges. The isolated pentagons are converted back to hexagons by additional deposits, and open-ended growth can continue. We should caution that although the Tersoff-Brenner potential gives reliable estimates for the

elastic constants of graphite and nanotubes [23], we expect some differences between our calculated crossover (~3 nm) and that observed experimentally (~2.2 nm, see Ref. [1]), due to a wide range of possible helicities, growth kinetics, and the presence of nearby tubes and bundles in the experiments.

All arguments presented so far rested solely on energy considerations. To simulate kinetic effects at high growth temperatures, e.g., bond breaking and bond switching, we have performed classical molecular dynamics (MD) simulations at 3000 K using the Tersoff-Brenner potential. Although high-energy structures might form initially, annealing for a few nanoseconds does result in the lowest energy structures discussed above. Our MD simulations with closed tubes have resulted in essentially disordered structures with many pentagonal and heptagonal defects [24]. These defects do not anneal out during our simulation time, thus preventing tube growth, in agreement with experimental evidence for open-ended growth [3].

In summary, an accurate calculation of the electric field at the tube tip followed by *ab initio* MD simulations show that the field cannot be the critical factor that keeps the tubes open during growth. The mechanism of growth was further investigated through total-energy calculations and molecular dynamics, using a realistic three-body potential. It was found that the addition of atoms and small clusters to the tube edge leads to the formation of hexagons and isolated pentagons for tube diameters greater than 3 nm. Adjacent pentagons nucleate at tubes of smaller diameters, leading to highly curved structures and eventually to tube closure after additional depositions. The energetics of these adatom structures may thus explain the lack of observation of narrow tubes in noncatalytic growth.

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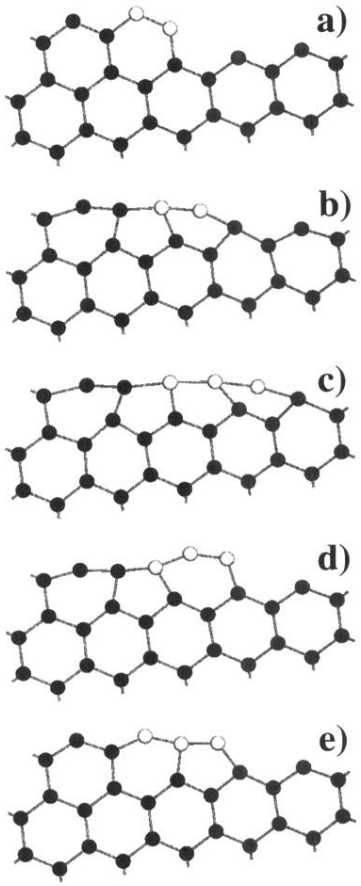

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