

Nucleation of Single-Walled Carbon Nanotubes

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The nucleation pathway for single-wall carbon nanotubes on a metal surface is demonstrated by a series of total energy calculations using density functional theory. Incorporation of pentagons at an early stage of nucleation is energetically favorable as they reduce the number of dangling bonds and facilitate curvature of the structure and bonding to the metal. In the presence of the metal surface, nucleation of a closed cap or a capped single-wall carbon nanotube is overwhelmingly favored compared to any structure with dangling bonds or to a fullerene.

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Single wall carbon nanotubes (SWNTs) can be produced under a variety of conditions including laser ablation [1], arc discharge methods [2,3], and chemical vapor deposition (CVD) [4]. Numerous theories have been proposed for the growth mechanism, some from the vapor phase [5–7], others from a condensed phase [8,9], with growth taking place either at the tip [10,11] or the root [8,9]. In one study of CVD growth, transmission electron microscopy observations showed SWNTs to nucleate around small metal nanoparticles. In this case no larger metal particles were present and the tube diameter was determined by the nanoparticle size [12]. In contrast, another recent study [13] suggested that the three growth methods have a common growth mechanism based on the vapor-liquid-solid model [14]. Microscopy evidence was presented showing SWNTs and bundles to nucleate from larger particles. These authors also reported calculations suggesting that once a capped nanotube is nucleated, growth can be effected through diffusion of surface carbon atoms to the root.

Electron microscopy has therefore established that nanosized clusters are not essential for nucleation of SWNTs and that nucleation occurs on the metal catalyst particles. An example from our own work is shown in Fig. 1, where SWNTs have formed *exclusively* during laser ablation despite the large range of catalyst particle sizes seen in the *Z*-contrast image. The high-resolution phase-contrast image shows that the catalyst particles are the source of the tubes. Such observations imply that the nucleation occurs at the surface of the liquid metal-carbon droplet by agglomeration of carbon atoms from inside the drop, or, if the particle is solid, from carbon diffusing across the particle surface.

Prior atomistic calculations of nucleation have not so far examined the nucleation process in detail. Calculations have investigated the rolling of a preexisting graphite double layer into a tube [15], the closure of an open

tube [16], and the emergence of a capped SWNT [11] from a continuous graphite sheet. Classical nucleation theory has had some successes [9,17,18], but many of the critical energies involved can only be crudely estimated. In addition, the pathway is usually assumed to involve growth of a flat sheet to a critical size at which point it becomes energetically favorable to transform into a tube. Our results do not support such a pathway.

In this Letter we report first-principles calculations which show that pentagons are introduced at the *initial* stage of nucleation. The energy cost of incorporating the pentagons is outweighed by the reduction in energy associated with dangling bonds at the periphery of the nucleus. We compare various forms of possible nuclei on the surface of Ni metal and establish that a cap or capped tube is energetically preferred over a graphene sheet, a fullerene, or an open tube. The calculations demonstrate not only that SWNT will result from the vapor-liquid-solid mechanism, on cooling a liquid metal-carbon drop through the eutectic point, but also from condensed phases during laser ablation [19] or subsequent reannealing [20]. The calculations also explain why bundles or even multiple bundles of SWNT can form on a single catalyst particle, as observed [21]. Once a nanotube is nucleated, it can move freely on a liquid metal surface, and nearby tubes can be assembled immediately into bundles driven by van der Waals interactions.

Calculations were performed [22] using the local-density approximation [23] for the exchange-correlation potential, ultrasoft pseudopotentials [24] with a plane wave energy cutoff of 380 eV, and the Monkhorst-Pack scheme [25] for Brillouin zone *k*-point sampling. The all-bands scheme [26] was used for electronic minimization and the Broyden-Fletcher-Goldfarb-Shanno scheme [27] for ionic relaxation. The exchange-correlation potential was represented using the Ceperley-Alder form [28].

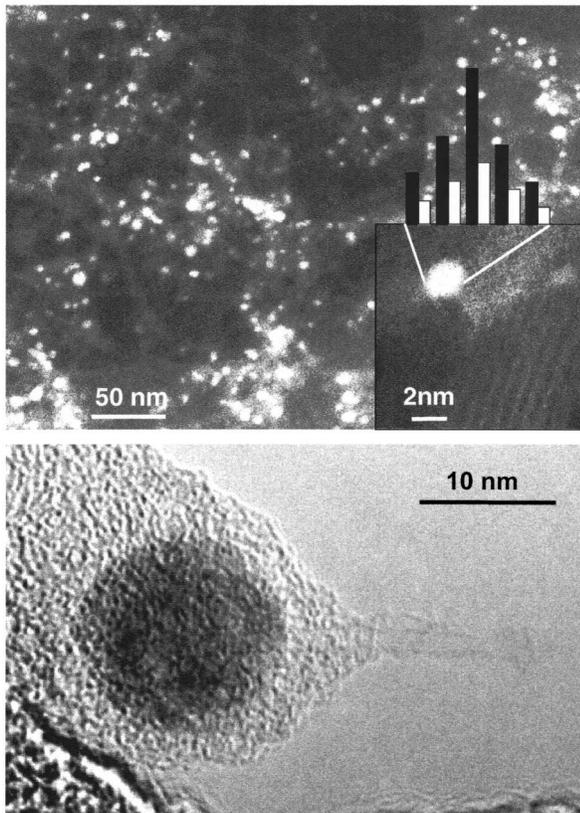


FIG. 1. Z-contrast image of Co/Ni catalyst particles in laser ablation grown SWNTs. The inset image shows one of the smallest nanoparticles found ~ 2 nm diameter. The histogram compares the Co (black) and Ni (white) composition profiles across the 2 nm particle determined by electron energy loss spectroscopy. (b) High resolution TEM image of a SWNT emerging from a catalyst particle.

Our objective is to describe the pathway for the nucleation and evolution of the optimal carbon structure on a metal surface. It is not feasible to determine the minimum energy configuration as each additional carbon atom joins the evolving cluster since the number of permutations is enormous. Instead we performed total energy calculations on clusters comprising different numbers of pentagons and hexagons to establish the general nature of the nucleation pathway. For each structure, several initial positions were tried on a $\{100\}$ Ni surface and relaxed to determine the lowest energy. We express all energies as *excess* energies relative to the same numbers of C atoms in an infinite graphene sheet and of Ni atoms in a free Ni slab. In addition to determining the lowest energy configurations for different numbers of carbon atoms, we used static calculations to determine selected energy barriers. Finally, finite-temperature simulations were pursued at 1000 K for selected structures.

Figure 2 shows the excess energy per carbon atom relative to an infinite graphite sheet as a function of the number of carbon atoms n in the cluster. Each cluster is labeled p, h according to the number of pentagons p and

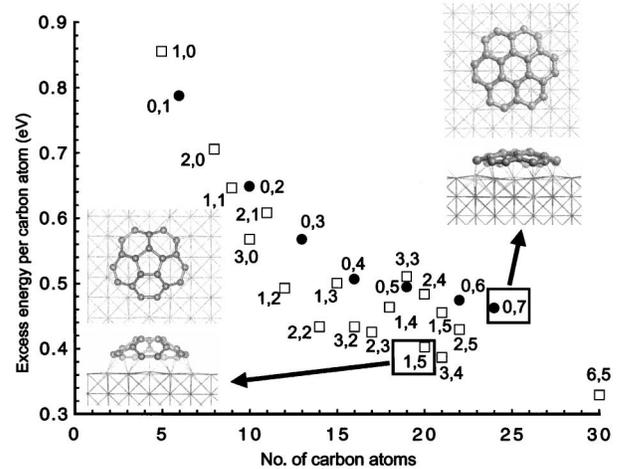


FIG. 2. Plot of the excess energy per carbon atom for various nuclei on Ni. Points are labeled p, h where p is the number of pentagons and h the number of hexagons in the structure. The insets show representative relaxed structures.

hexagons h . When the clusters are small, there is little difference in the excess energy per carbon atom. However, above ~ 10 carbon atoms there is a definite preference for structures containing pentagons. There are two reasons for this. First, among the structures built with the same (or similar) number of carbon atoms, those containing pentagons have fewer dangling bonds per atom, and second, they can deform into a dome to better saturate the dangling bonds at their edges, as seen in the insets. Energies shown are the lowest of several runs with different starting locations of the flakes. Charge transfer from C to Ni atoms was found to be smaller than 0.15 electrons per C atom at the edge of the structure. These results show clearly that it is favorable to incorporate pentagons during the initial stages of nucleation.

In order to check for possible kinetic constraints to the formation of the above structures we calculated energy barriers for selected processes. We confirmed the well-known fact that transformations of adjacent six- and five-membered rings to five- and six-membered rings entail large energy barriers ($\sim 4-5$ eV) [29,30]. On the other hand, test calculations suggest that the barrier is reduced substantially in the presence of a newly arriving C atom. For a few selected structures, molecular dynamics at 1000 K were carried out in order to check for finite-temperature effects. We found that among structures containing a given number of C atoms, those built with hexagons alone have higher excess free energy per C atom, confirming the conclusions we reached with the static calculations.

The 6,5 structure is the smallest radius hemispherical structure that can be formed but is already very large for density functional calculations. To handle larger structures we therefore move to a bond energy formulation based on the results of the previous density functional calculations. The total energy E_{total} is expressed as sums

of bond energies:

$$E_{\text{total}} = n_{\text{graph}}E_{\text{graph}} + n_{\text{dang}}E_{\text{dang}} + n_{\text{c-m}}E_{\text{c-m}} + n_{\text{cyl}}E_{\text{cyl}}(r) + n_{\text{sph}}E_{\text{sph}}(r), \quad (1)$$

where the respective energies are E_{graph} for a C-C bond in an infinite graphite sheet, E_{dang} for a dangling bond at the edge of a finite graphene sheet or a finite length of nanotube, $E_{\text{c-m}}$ for a carbon-metal bond, E_{cyl} for a C-C bond in a nanotube, and E_{sphere} for a C-C bond in a fullerene. The n_i denote the numbers of the i th-type bond [31].

This analysis shows that the energy cost involved in curvature is quite low: for a C_{60} molecule $E_{\text{sphere}} = 0.135$ eV and for an infinite (5,5) nanotube $E_{\text{cyl}} = 0.067$ eV. Both have the same radius r ; the energy cost of the C_{60} is double that of the cylinder due to the incorporation of pentagons. It is consistent with elasticity theory for curvature in two dimensions as opposed to one. For the carbon-metal bond energy we used a finite (5,5) nanotube between two Ni slabs, giving $E_{\text{c-m}} = 0.079$ eV. *All of these energies are small* compared to the energy of a dangling bond. At the edge of a graphene flake, we obtain $E_{\text{dang}} = 2.26$ eV, while at the edge of the nanotube, $E_{\text{dang}} = 2.0$ eV. The high energy of the carbon dangling bonds makes it energetically favorable to introduce pentagons at an early stage of nucleation. This is the primary factor driving the nucleation pathway.

As a test of accuracy we calculated the energy of a 30 atom hemispherical cap on Ni directly using density functional theory and also with the bond energy approximation. The difference between the two calculations is only 0.26 eV for the whole structure, or 0.009 eV per C atom, small with respect to any bond energy. These numbers are negligible when compared with the overall accuracy of first-principles calculations. We next used the bond energies to calculate the total excess energies of several possible forms of nuclei containing 60 carbon atoms, as shown in Fig. 3. For larger radius tubes and caps, the r dependence of $E_{\text{cyl}}(r)$ and $E_{\text{sph}}(r)$ was modeled

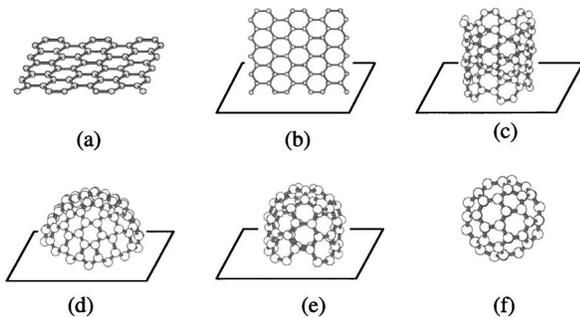


FIG. 3. Several typical configurations of 60 atom carbon nuclei: (a) an isolated flat graphite flake; (b) a flat graphite flake perpendicular to a metal surface; (c) an open ended 5,5 tube on metal; (d) a hemispherical cap on metal; (e) a capped 5,5 tube on metal; (f) an isolated C_{60} fullerene.

by $E(r) \propto 1/r^2$, which is consistent with explicit calculations for tubes [32] and with elasticity theory. Excess energies relative to an infinite graphite sheet are listed in Table I. The energetically favorable nucleus on a flat metal surface is the 0.95 nm radius cap, closely followed by the capped (5,5) tube with radius 0.67 nm. If we remove the metal, i.e., replace the metal-carbon bonds by dangling bonds, the excess energy of the capped tube becomes 32.6 eV. This energy is still less than that of a graphite flake (45.9 eV without metal) but is now *larger* than that of the fullerene. This result, in agreement with previous tight-binding calculations [33], explains the stability of fullerenes in the absence of metal.

To explore still larger structures we use these bond energies as the basis for a continuum calculation. A continuum model was constructed by replacing the energy per bond by the energy per unit area and the energy per unit edge length. We simulate the growth process by increasing the structure area and minimizing the excess energy with respect to the structure's radius and height. These calculations show that starting from a cap, it is favorable to increase its diameter up to 10 nm before increasing the length of the tube. However, such diameters are never seen in practice for single-wall tubes. We conclude, therefore, that in practice the diameter is determined by kinetic factors. The differences in excess energy per atom between the different structures shown in Fig. 2 are comparable to available thermal energies at 1000–2000 °C. Therefore, the various configurations are likely to be explored in the real system given sufficient time. However, as a structure grows, a kinetic limitation is likely to arise because of the increasing number of bond rearrangements that are necessary to explore all the possible permutations and find the global energy minimum. If the rate of arrival of carbon atoms exceeds the rate at which bonds in the cap can rearrange, then the radius of the cap can no longer increase, and carbon atoms will be added to the base of the cap. Now a SWNT will be extruded with a radius fixed by the kinetic constraint.

In summary, we have demonstrated that pentagons are incorporated in the early stages of nucleation in order to

TABLE I. Total energy of different structures. The configurations [(a)–(f)] correspond to the structures in Figs. 3(a)–3(f), respectively.

Configurations	Flake (a)	Flake (b)	Open tube (c)	Large cap (d)	Capped tube (e)	C_{60} (f)
n_{graph}	80	80				
n_{cyl}			80			
n_{sphere}				83	40	90
n_{dang}	20	14	10			
$n_{\text{c-m}}$	0	6	10	14	10	
E_{total} (eV)	45.9	32.1	31.3	16.8	17.3	24.0

reduce the energy cost associated with dangling bonds. Whether nucleation occurs from a saturated carbon-metal liquid by the vapor-liquid-solid mechanism, or by coalescence of carbon on the metal surface, caps or capped tubes are the preferred form of nucleus. As the structure grows, the increasing activation barrier to bond rearrangements in the cap eventually prohibits an increase in radius, and a tube is extruded. At this stage, further growth occurs only at the root, leading to the narrow size distributions observed experimentally.

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