

Catalytic Growth of Single-Wall Carbon Nanotubes: An *Ab Initio* Study

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We propose a catalytic growth mechanism of single-wall carbon nanotubes based on density functional total energy calculations. Our results indicate nanotubes with an “armchair” edge to be energetically favored over “zigzag” nanotubes. We also suggest that highly mobile Ni catalyst atoms adsorb at the growing edge of the nanotube, where they catalyze the continuing assembly of hexagons from carbon feedstock diffusing along the nanotube wall. In a concerted exchange mechanism, Ni atoms anneal carbon pentagons that would initiate a dome closure of the nanotube. [S0031-9007(97)02791-9]

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Single-wall carbon nanotubes, consisting of a graphene sheet seamlessly wrapped to a cylinder, have been produced in the outflow of a carbon arc [1–5] and in even higher yield by the laser vaporization technique [6–8]. In both cases the selective formation of nanotubes was triggered by enriching the graphite source material with a transition metal catalyst. These nanotubes have a typical diameter of only ≈ 13.8 Å [6], but can bundle up to form ropes [6,9–13] that are as long as tenths of a millimeter. Samples obtained with the high-yield laser vaporization technique do not contain any remaining metal catalyst in the tubes [6]. In spite of the enormous progress in the synthesis, theoretical understanding of the nanotube growth lags behind.

Probably the most intriguing problem is to understand the microscopic mechanism and optimum conditions for the formation of single-wall nanotubes rather than the energetically more favorable fullerenes. The key issue will be whether the metal catalyst plays a passive role, preventing a premature dome closure, or an active role, by assisting in the assembly of carbon hexagons at the growing edge. We would like to understand not only the intermediate structures that evolve at the growing tube edge, but also the dynamics of the carbon feedstock supply and the catalyst-assisted growth process.

We address these topics by performing density functional theory total energy calculations for a growing single-wall nanotube in contact with a Ni catalyst particle. We propose that the carbon feedstock in the atmosphere, consisting of large carbon aggregates under the experimental conditions [6], is first catalytically broken down to smaller clusters [14]. These small aggregates adsorb on the nanotube wall and diffuse to the growing edge. We will show that atomic nickel that is strongly bound but still very mobile at the edge locally inhibits the formation of pentagons and, in a concerted exchange mechanism, assists in the formation of carbon hexagons. Tube closure is initiated when several catalyst atoms aggregate and detach from the growing edge.

The nucleus of a growing nanotube is a cylinder that is capped on one side and open at the other side. Total energy

calculations indicate that the equilibrium cylinder diameter for a system containing few hundred atoms is ≈ 14 Å [6]. Global structural changes modifying the diameter do not occur beyond this size due to the fast tube growth rate. We model the growing edge of the carbon nanotube by a graphite flake containing 20–30 atoms. The low concentration (<1%) of the transition metal catalyst in the graphite material and the high temperatures in the experiment suggest that the catalyst may occur as single atoms which bind strongly to the exposed edge [15,16].

Our results are based on density functional total energy calculations, as implemented in the DMol code [17,18], for a tube fragment with a Ni atom attached to the edge. Both the local density approximation (LDA) and the generalized gradient approximation (GGA) [19] are used to describe exchange and correlation. We use the von Barth and Hedin parametrization [20] of the exchange-correlation energy in LDA, and expand the all-electron Kohn-Sham wave functions in a local atomic orbital basis. In the double-numerical basis set [18], the $C2s$ and $C2p$ orbitals are represented by two basis functions each, and a $3d$ type wave function on each carbon atom is used to describe polarization. The Ni atom is treated in the analogous way. The $C1s$ orbital and the Ar core orbitals of Ni are frozen throughout the calculations. The convergence criterion for structure optimization is that all forces be ≤ 0.001 Ry/Å. The energies are converged to 10^{-4} eV.

From the point of view of stability, achiral nanotubes with the lowest edge energy should prevail. We determined the edge energies of zigzag and armchair nanotubes from a careful total energy comparison between structurally relaxed graphite flakes of different sizes, taking special care to avoid finite size effects. The equilibrium bond length in nanotubes is close to the graphite value $d_{CC} = 1.42$ Å. The average distance between twofold coordinated atoms at the exposed edge is 2.13 Å in armchair nanotubes and 2.46 Å in zigzag nanotubes. The calculated edge energies are 2.20 eV per edge atom (or 10.31 eV/nm) for armchair nanotubes and 2.99 eV per edge atom (or 12.14 eV/nm) for zigzag nanotubes. The armchair edge owes its extra stability to unpaired

electrons which help to form a stable, 1.23 Å long triple bond between adjacent sites. The unpaired electrons at the edge of a zigzag nanotube, on the other hand, attempt to establish a double bond with their neighbors, resulting in a bond length of 1.37 Å. Thus an armchair nanotube nucleus is preferred by 0.79 eV per edge atom (or 1.43 eV/nm) over the nucleus of a zigzag nanotube, assuming the same tube length and diameter. Together with the above total energy arguments suggesting ≈ 14 Å for the equilibrium tube diameter, the same as that of the C_{240} fullerene, we believe the (10,10) nanotube [21] to prevail under the experimental conditions of Ref. [6] and focus on the growth of armchair nanotubes in the following.

A central point to address is the role of the metal catalyst that is a necessary prerequisite for the formation of single-wall nanotubes. The primary role of the catalyst is obviously to prevent carbon pentagons from forming at the growing edge that would initiate dome closure. In order to anneal such defects efficiently, the adsorption energy of the catalytic particle has to be comparable in strength to the carbon bonds in the nanotube. A strong adsorption bond will also prevent the catalytic particle from desorbing. On the other hand, the catalytic particle has to be sufficiently mobile to anneal these defects before they are incorporated in the growing structure.

In Fig. 1 we show the adsorption energy and equilibrium height of a Ni atom [15] at the exposed edge of an armchair nanotube as a function of its position along the edge. Our LDA calculations, based on fully relaxed geometries of Ni interacting with a C_{22} graphite flake, suggest a strong adsorption bond of -6.4 eV at both the arm and the seat sites. We found this value to be converged with respect to the flake size, since saturating by hydrogen those flake edges that are embedded in the graphitic lattice of the tube resulted in lowering the Ni adsorption energy by a mere 0.1 eV [22]. We found that using GGA instead of LDA for the exchange-correlation energy re-

sulted in a uniform lowering of the adsorption energy by 1.7 eV, independent of adsorption site [22]. In view of the strong Ni-tube bond, Ni desorption from the exposed edge is very unlikely at the experimental temperature of ≈ 1200 °C. In comparison to the binding energy, the activation barrier for Ni diffusion along the tube edge $\Delta E \approx 1.0$ eV is quite low, which warrants its high mobility. Quantitatively similar values are obtained also for other metals, such as Co [23].

With the potential energy profile at hand, we used transition state theory [24] to estimate the diffusion rate of Ni along the tube edge. For the typical experimental temperature of 1200 °C we estimated the diffusion coefficient to be $D \approx 2 \times 10^9$ Å/s. With an estimated growth rate of ≈ 0.1 mm/s [6], a Ni atom would be expected to “scoot” around the tube edge up to 10^2 times before a new “ring” would grow at the end. Even though structural imperfections at the growing edge will slow down the Ni atom significantly, the estimated high diffusion rate suggests that even a single Ni atom per nanotube should be almost instantly available to anneal any forming defect. Indeed, using a mere 1% admixture of transition metal in the carbon source material resulted in the high yield of nanotubes reported in Ref. [6].

The activation barrier for the diffusion of carbon atoms along the edge, $\Delta E \approx 2.4$ eV, is much higher than that of Ni. The corresponding diffusion coefficient is lower by a factor of 10^5 compared to Ni. Consequently, carbon is essentially immobile and not capable of spontaneously annealing defects.

In order for a tube to grow, carbon feedstock from the atmosphere has to be transported to the growing edge. We will assume that large carbon aggregates are catalytically broken down to clusters of few atoms [14] that adsorb on the growing nanotube, more probably at the tube surface than directly at the tube edge. The cool inert gas used in the synthesis increases the sticking coefficient by carrying away excess energy from the adsorption site. In the following, we will consider the diffusion of individual carbon atoms [25] along the tube surface and their final inclusion in the growing edge from an energetic point of view.

Our LDA results for the interaction of carbon atoms with the growing nanotube, based on completely relaxed geometries, are summarized in Fig. 2. The weakest adsorption bond forms at the hexagon center (C site), with a small binding energy $E_b(C) = -0.64$ eV and a bond length $d(C) = 1.97$ Å to its nearest neighbors at the surface. The carbon adsorption bond is stronger at the on-top site (T), with $E_b(T) = -1.65$ eV, and the bridge (B) site between two carbon atoms, $E_b(B) = -1.78$ eV. The respective adsorption bond lengths are $d(T) = 1.51$ Å and $d(B) = 1.54$ Å.

The small binding energy difference between these inequivalent sites suggests that carbon atoms can glide efficiently along the tube surface until they reach the reactive edge and stick to it. Presence of unsaturated bonds at the edge is the cause not only of a high adsorption energy, as

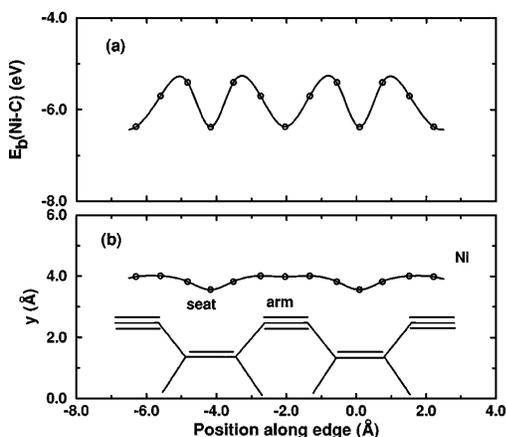


FIG. 1. (a) The binding energy E_b of a Ni atom along the “armchair” edge of a carbon nanotube. (b) Equilibrium height y of a Ni atom along the “armchair” edge with respect to the third layer of carbon atoms.

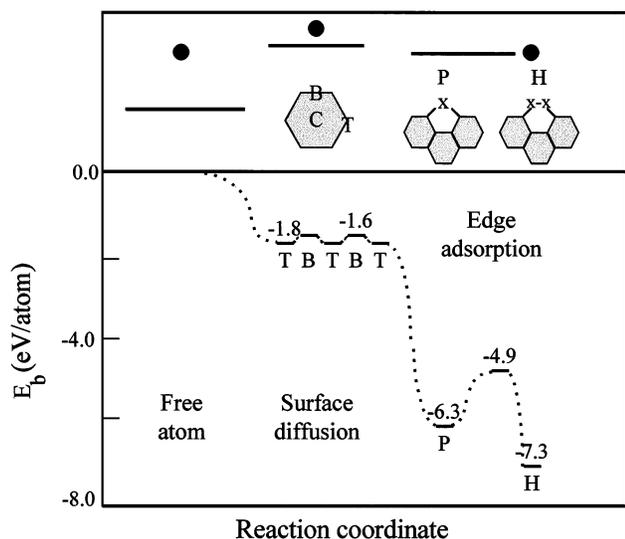


FIG. 2. The binding energy E_b of a carbon atom during its reaction with the growing nanotube. As indicated by the schematic inset, we consider surface adsorption from gas phase, then diffusion along a trajectory containing bridge (B), center (C), and on-top (T) sites towards the edge, followed by adsorption at the seat site, forming either a pentagon (P) or a hexagon (H).

seen in Fig. 2, but also a low mobility of adsorbed carbon atoms along the edge. Isolated carbon atoms may adsorb either in the arm site, or form a pentagon (P) when adsorbing at the seat site. As mentioned above, the activation barrier for two carbon atoms, forming pentagons at adjacent seat sites, to recombine to a single hexagon is quite high, as shown in Fig. 2. More likely than isolated atoms, we can expect small clusters (such as short chains that prevail at high temperatures [26,27]) to attach to the growing edge where they can fragment. In the ideal case, dimers can complete hexagons upon adsorption at the seat site. Other fragments, such as longer chains or rings [28], may form defects including pentagons. The crucial role played by the catalytic particles is to anneal efficiently these defects before they may cause the nanotube growth to terminate.

In the following, we discuss the detailed catalytic mechanism leading to the annealing of a pentagon defect that could initiate dome closure of the tube. Other defects are far less important for the termination of growth, since the corresponding structures are typically unstable and reactive and may eventually be annealed. Only a nanotube terminated by a perfect dome containing six pentagons is sufficiently inert to resist any structural changes.

The intermediate states and energetics associated with an intriguing concerted exchange mechanism of the catalytic process are given in Fig. 3. We begin with two carbon atoms diffusing along the surface to the tube edge that contains a Ni atom, as shown in Fig. 3(a1). In this (and many different scenarios) one of the carbon atoms may gain 4.5 eV by forming a pentagon defect, shown in Fig. 3(a2). Owing to the high mobility of Ni at the edge,

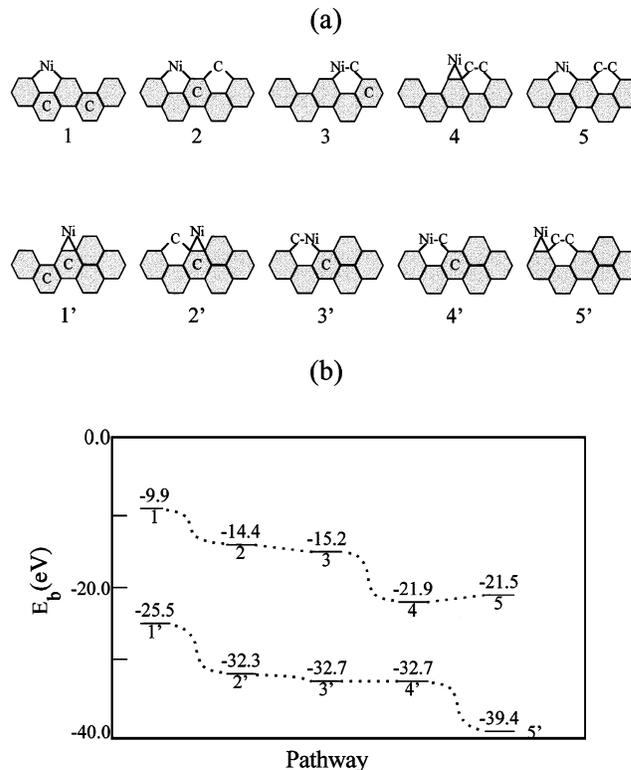


FIG. 3. (a) Schematic diagram of intermediate steps involved in the catalytic annealing of pentagon defects at the growing nanotube edge by a concerted exchange mechanism, leading to defect-free growth. (b) Corresponding binding energies of the two carbon atoms and one Ni atom to the nanotube.

the catalyst reacts with the adsorbed carbon to form a hexagon, shown in Fig. 3(a3), before the pentagon defect would be stabilized in the growing carbon structure. This reaction step, where the Ni masquerades as a carbon, yields another energy gain of 0.8 eV. It is analogous to the formation of metallacycle structures which are well known in organometallic chemistry [29]. Of course, this intermediate structure is less stable than a perfect carbon hexagon at the growing edge. We believe that an incoming carbon atom will push out the substitutional Ni atom. This step gains the system a substantial energy of 6.7 eV and closes the catalytic cycle, as depicted in Fig. 3(a4). Because of its weak attachment energy of 0.4 eV to the newly formed hexagon [inferred from the geometries in Figs. 3(a4) and 3(a5)], a value well below the activation barrier for diffusion, the Ni atom may now continue its diffusion about the tube edge to assist in the catalytic annealing of other defects.

The situation, where a new pentagon defect forms prior to Ni leaving the adsorption site shown in Fig. 3(a4), is depicted in Figs. 3(a1') and 3(a2'). Also in this situation, Ni readily substitutes for a second carbon atom at the pentagon defect site, as shown in Fig. 3(a3'). A local rearrangement and a final substitution of Ni by a second carbon atom, illustrated in Figs. 3(a4') and 3(a5'), close this alternate catalytic cycle. We note that both catalytic

processes are strictly exothermic and occur with no activation barriers, suggesting a high reaction rate.

Of course, the Ni catalyst can efficiently anneal defects other than those discussed above. Should a carbon atom adsorb in the arm site adjacent to a pentagon defect, Ni may first form a metallacycle, such as in Figs. 3(a3) or 3(a3'). Our calculations indicate that in such a case, the two adjacent carbon atoms spontaneously move to the seat site, forming a perfect hexagon, while pushing the Ni catalyst atom aside to the geometry depicted in Fig. 3(a4) or 3(a5'). This exothermic step also provides the adsorbed Ni atom with substantial momentum promoting its "scooter" motion [30].

With a nonvanishing concentration of Ni atoms in the atmosphere, several catalyst atoms will eventually aggregate at the tube edge, where they will coalesce. We found the adsorption energy per Ni atom to decrease by 0.5 eV in Ni₂ adsorbed at the seat site, confirming the general trend for the adsorption bond to weaken with increasing size of the adsorbed cluster. We expect the ability of Ni clusters to anneal defects to decrease with their increasing size, since they will gradually become unreactive and less mobile. Eventually, the adsorption energy of the cluster will decrease to such a level that it will peel off from the edge. In absence of the catalyst at the tube edge, defects can no longer be annealed efficiently, thus initiating dome closure. This mechanism is consistent with the experimental observation that no observable metal particles are left in the grown tubes [6,21]. This also suggests that a too high concentration of the metal catalyst will be detrimental to the formation of long nanotubes.

In summary, we have studied the catalytic growth of single-wall carbon nanotubes using the density functional formalism. Based on energy arguments during the early growth stage, we found "armchair" nanotubes with a diameter of ≈ 14 Å to be the preferred structures. We found that catalytic Ni particles likely adsorb as atoms at the growing edge. While their large adsorption energy holds them strongly attached to the nanotube, the relatively small diffusion barrier of ≈ 1 eV gives them a high mobility along the tube edge. Using a concerted exchange mechanism, adsorbed Ni atoms catalyze the continuing assembly of carbon hexagons from carbon feedstock diffusing along the nanotube wall while efficiently annealing pentagon defects that would otherwise lead to a premature dome closure of the nanotube.

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