Growth of Carbon Nanotubes on Metal Nanoparticles: A Microscopic Mechanism from *Ab Initio* Molecular Dynamics Simulations

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(Received 8 March 2005; published 26 August 2005)

We report on *ab initio* molecular dynamics simulations of the early stages of single-walled carbon nanotube (SWCNT) growth on metal nanoparticles. Our results show that a $sp2$ bonded cap is formed on an iron catalyst, following the diffusion of C atoms from hydrocarbon precursors on the nanoparticle surface. The weak adhesion between the cap and iron enables the graphene sheet to "float" on the curved surface, as additional C atoms covalently bonded to the catalyst "hold" the tube walls. Hence the SWCNT grows capped. At the nanoscale, we did not observe any tendency of C atoms to penetrate inside the catalyst, consistent with total energy calculations showing that alloying of Fe and C is very unlikely for 1 nm particles. Root growth was observed on Fe but not on Au, consistent with experiment.

DOI: 10.1103/PhysRevLett.95.096103 PACS numbers: 81.07.De, 68.55.Ac

Controlling the growth of carbon nanotubes (CNT) on metallic catalysts is an essential prerequisite for their nanoscale manipulation and their use in technological applications [1]. Among the various CNT synthesis routes proposed in the literature, chemical vapor deposition (CVD) has attracted a widespread interest, as it opens the way to a highly controlled nanotube production on designed architectures [2]. In the CVD process, metal catalyst nanoparticles supported by an inert substrate are placed in a mixed flow of hydrocarbons (usually methane) and other gases, e.g., hydrogen. The growth process is often described as driven by a supersaturation of the C-metal solution followed by C segregation and emergence of carbonaceous structures from the catalyst surface. The nature of these structures, ranging from amorphous carbon to single-walled carbon nanotube (SWCNT) and multiwalled carbon nanotube, depends on the type and size of the catalyst, the type of substrate, and specific thermodynamic conditions.

The physical properties of the substrate and of the catalyst are known to play a key role in CNT formation, and electron microscopy has shown that growth is an extremely complex and diverse process, which can occur either by the tip [3] or by the root [4] of the tube, and with a tube diameter that does not necessarily match that of the catalyst particle [5]. In particular, the TEM results reported in Ref. [3] show how multiwall nanotubes grow out of 6 nm nickel nanoparticles following a tip-growth mechanism, and those obtained by Li and collaborators [4] show a root growth process on small (1–2 nm) Fe catalysts, leading to SWCNT. This shows that growth may occur differently, depending on the catalyst size.

Recent theoretical studies have tried to rationalize some of the factors influencing the formation of CNTs. Atomistic calculations suggest that only multiwalled nanotubes may grow with an open end [6]. Other static, *ab initio* calculations have shown that the formation of a carbon pentagon was preferred over that of a hexagon on a flat catalyst surface [7], and the formation of some fivefold and sixfold C rings on the surface of supersaturated cobalt clusters was observed in Ref. [5]. These authors also reported simulations of SWCNT growth on a flat Co surface, where they considered half of a C_{60} molecule placed on a supersaturated substrate, with additional C atoms diffusing and eventually being incorporated at the root of the half C_{60}. Empirical calculations using Lennard-Jones and Brenner potentials could simulate the emergence of SWNT from small metallic particles and emphasized the crucial effect of temperature and size [8,9].

However, no theoretical investigation has been reported so far that addresses the dynamical formation process of SWCNT on metal nanoparticles from first principles, or without the *a priori* assumption of supersaturation of carbon into the catalyst.

In this Letter, we describe the results of *ab initio* molecular dynamics (MD) simulations [10,11] aimed at understanding the early stages of CNT's growth on metal nanoparticles. In particular, we considered a 1 nm Fe catalyst, which has been shown to lead to the highest SWCNT production rate in CVD growth, when placed on an alumina substrate [14], and we compared our results with those obtained by simulation deposition on gold, after dissociation of hydrocarbons. We find that SWCNTs grow capped on Fe, with no significant diffusion of C into the catalyst. Growth was not observed on gold; the difference between the results obtained for Au and Fe indicate that the relative binding energy of $sp2$ bonded C atoms embedded in carbonaceous fragments and of lower coordinated C bound to the catalyst plays an important role in tube growth on small transition metal nanoparticles.

Our computer experiments were designed as follows: we considered a 1 nm Fe nanoparticle (55 atoms) with core atoms in fcc positions. The γ-phase (fcc) is observed in bulk Fe above 1189 K and is characteristic of iron nanoparticles as well [15]. About half of the nanoparticle surface atoms were passivated with H to mimic the presence of a supporting surface. The substrate atomic structure could not be explicitly considered in our simulations, as it would have been prohibitively expensive from a computational point of view. Hydrogen passivation has a desirable steric effect, as the passivated surface is not available to provide diffusion paths to carbon atoms. In simulations where the nanoparticle was not appropriately passivated, we observed its complete encapsulation in a carbon cage, in agreement with Ref. [16]. This points at the importance of a substrate preventing C diffusion all around the nanoparticles in the growth process, and it is consistent with experimental results reporting different growth rates depending on the nature of the substrate [14,17,18].

In our calculations, consistent with gas-phase species concentration studies [19], we assumed that the dissociation of C precursors, e.g., methane, on the catalyst would account for the presence of C atoms in the vicinity of the surface and that H atoms would readily evaporate as a molecular gas and leave the system. We randomly added 1 C every ~0.3 ps close to surface Fe atoms, which were not yet linked to any other C or H. This is a rather high deposition rate, dictated by the computationally demanding nature of *ab initio* calculations for large systems containing transition metals. The time interval between additional C depositions is sufficiently long, however, to allow for C atoms to diffuse over at least one Fe-Fe bond length and eventually bind to other C atoms. In cases where we forced an even faster deposition rate, we observed the formation of carbon chains, or filaments, that remain attached to the catalyst on one side and are freely floating in vacuum on the other side. This is due to the impossibility to anneal structural defects before further carbon atoms are injected into the system, over a short simulation time.

To understand in detail the early stages of the growth mechanism, we carried out simulations starting from different initial conditions of carbon coverage on iron nanoparticles [20]. These are shown in Fig. 1. When starting from well separated C atoms [equally spaced for simplicity; see Fig. 1(a)] on the free surface of the half-passivated Fe cluster, we observe fast diffusion of the C atoms (over the 10 ps of our simulation), until they can connect to other carbons [see Fig. 2(a); the temperature is thermostatically adjusted to 1200 K]. Dimers are formed first, then short chains, which eventually interconnect so as to form a $sp2$-bonded graphene sheet. While onefold and twofold coordinated C remain covalently bonded to Fe surface atoms, threefold coordinated atoms (at C-chain junctions) are only weakly bound to the catalyst surface. The remaining undercoordinated C atoms injected into the system bind together until they reach an $sp2$ configuration. In that process, some rings (fivefold and sixfold) appear [see Fig. 2(a)].

Ultimately, a network of $sp2$ bonded carbons will extend over the free catalytic surface [see Fig. 2(b)]. This sheet is composed of pentagons and hexagons to accommodate the surface curvature. Some defects initially present in the sheet do anneal with time; for instance, squares, heptagons, or higher polygonal defects disappear after a few ps simulation runs at 1200 K. The sheet formed in this way is weakly attached to the iron surface and tends to oscillate during the cap formation. The cap remains attached to the catalytic particle due to the C atoms at the edge of the sheet, which are covalently bonded to the metallic surface [see Fig. 2(c)].

The observed growth process is largely independent of the initial C coordination. If dimers are deposited on the catalyst surface, growth proceeds in the same way as with isolated C atoms, following three basic steps, represented in Fig. 3: diffusion, interconnections to form the $sp2$ cap, then root incorporation for the wall growth.

Interestingly, during our short simulations, we never observed any tendency of carbon atoms to plunge into the metallic cluster. This indicates that, at the nanoscale, diffusion of C atoms at the surface is much faster than any process leading to incorporation inside the catalyst, at least for the 1 nm metallic particle considered here. Although

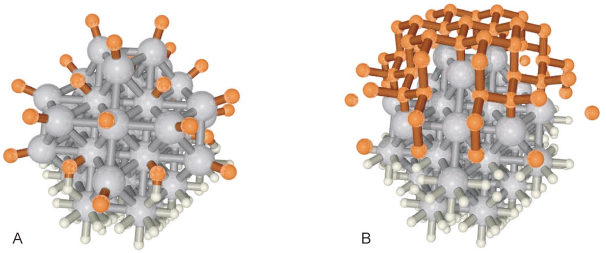

FIG. 1 (color). Different initial configurations chosen to start molecular dynamics simulations of CNT growth on metallic nanoparticles. Metal atoms are represented in gray, carbon atoms in pink, and hydrogen atoms in light white. (a) Equally spaced C atoms are placed on the catalyst; (b) C atoms are placed in the diamond lattice position on top of the metallic nanoparticle.

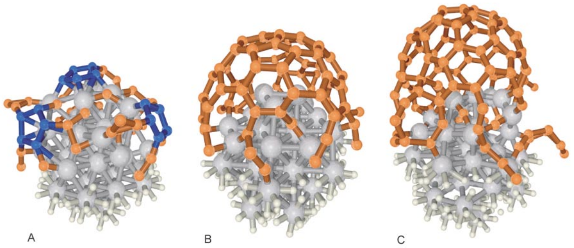

FIG. 2 (color). (a) This snapshot from *ab initio* simulations of the early stages of SWCNT growth on a 1 nm Fe catalyst shows that after diffusion of C atoms on the metallic surface and formation of C-C bonds, pentagons and hexagons appear on the surface (highlighted in blue). Color code is the same as in Fig. 1. (b),(c) Snapshots of the growth process of a SWCNT on a 1 nm Fe nanoparticle (55 atoms), as observed in *ab initio* molecular dynamics simulations.

much longer simulations would be needed to clearly exclude the occurrence of a Fe-C mixture prior to growth, our results show that the presence of a solid Fe-C solution and hence supersaturation-segregation processes are not needed for the growth process on small metal nanoparticles, and most likely they do not occur [21].

In order to substantiate these findings, we have analyzed the miscibility of C and Fe at the nanoscale by carrying out a series of total energy calculations at zero T. We have compared the relative stability of a Fe_{43} nanoparticle (fcc) with 1 C atom at the surface, and that with 1 C in the core. Total energy differences after relaxation unambiguously show that it is much more favorable for a C atom to sit at the surface than in the core [22]. This implies that, although it is possible to alloy up to 4 C atoms for every 55 Fe atoms in the austenite (fcc) phase of bulk Fe, the energetic of the Fe-C system is different at the nanoscale, where the surface to volume ratio is very large. These energy differences are expected to depend on the size of the catalyst, with the smaller nanoparticles being the least likely to incorporate any C during growth.

To rationalize the role of the catalyst in the growth process, we carried additional simulations on a 1 nm Au nanoparticle [Fig. 1(a)]. Although experimentally, gold is known not to be a good catalyst, we carried out simulations to verify that, indeed, we obtain agreement with experiment and our calculations are not affected by constraints such as H passivation or high deposition rates. On Au, once C dimers or chains are formed, they readily leave the catalyst surface as their interaction with the nanoparticle is not strong enough to allow for graphenelike fragments to form and bind. Therefore growth cannot occur. We also carried out a series of simulations starting from a preformed C monolayer [Fig. 1(b)]. We found that a cap forms by $sp2$ hybridization but then detaches from the gold surface after several vibrations (simulation time of about 2 ps).

The influence of the catalyst on the tube growth can be further analyzed by considering small model systems. We performed several computer experiments using 13 atom metallic clusters (fcc structure, either Fe or Au) interacting with carbonaceous fragments ($C_{13}H_9$ and $C_{10}H_8$) and with single C atoms. We relaxed the atomic structure of the clusters, passivated their surface in the same fashion as for the 1 nm particles used in the dynamical simulations, and computed binding energies between the C fragments and the cluster. These model computations also allowed us to explicitly include spin polarization effects in our calculations and to test the sensitivity of our results to the chosen plane-wave basis cutoff $[E_{\mathrm{cut}}]^2$ [23]. The trends for binding energies described below are robust with respect to both tests (spin and E_{cut}).

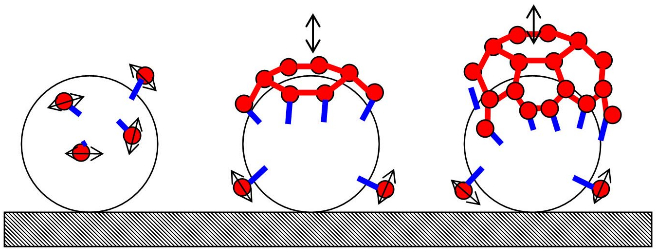

FIG. 3 (color online). Schematic representation of the basic steps of SWCNT growth on a Fe catalyst, as observed in *ab initio* simulations. (a) Diffusion of single C atoms (red spheres) on the surface of the catalyst. (b) Formation of an $sp2$ graphene sheet floating on the catalyst surface with edge atoms covalently bonded to the metal. (c) Root incorporation of diffusing single C atoms (or dimers).

We find that the binding energy of a single atom to the metal cluster is much larger for Fe than for Au (7.41 vs 2.91 eV), and the binding energy of graphenelike fragments is very small for Au (less than 0.01 eV/carbon) while it increases more than an order of magnitude in the case of Fe (0.05 eV/C for $C_{13}H_9$, 0.04 eV/C for $C_{10}H_8$). These results suggest that SWCNT growth may occur in the case of iron, where the covalent bond between a single C and a catalyst surface atom is the strongest and the adhesion of an $sp2$ bonded C on the catalyst surface is non-negligible, compared to the growth T. On gold, however, the graphene adhesion energy is negligible (compared to KT at 1200 K) while covalent bonding is significantly smaller than for carbide formers such as Fe. As a consequence, C atoms are not bound to the metal particle for a time long enough to allow for defect annealing and tube formation.

In summary, we have presented *ab initio* MD simulations of the early stages of SWCNT growth on small iron nanoparticles. We have shown that, after the formation of a curved $sp2$ bonded carbon sheet (the cap) by fast diffusion of single C atoms on the curved metal surface, growth occurs from the root. We did not observe any penetration of carbon atoms into the catalyst, and thus no supersaturation-segregation phenomenon was necessary for growth to occur, consistently with total energy calculation on the miscibility of C and Fe at the nanoscale. Root growth was observed on Fe but not on Au, consistent with the experiment and with binding energy calculations for small carbon fragments. Our results, combined with several experimental observations and previous calculations [5], point at the difference between growth processes occurring on nanocatalysts and on bulk surfaces, and they highlight the fact that details of the growth process depend on the nanocatalysts size.

We thank Professor Hongjie Dai for fruitful discussions, and J. Y. R. thanks the FNRS and the Region Wallonne (NOMADE Contract No. 115052) for their support. This work was performed under the auspices of the U.S. Department of Energy at the University of California–Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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[11] We use a plane-wave basis with $E_{\text{cut}} = 35$ Ry and Hamann-type pseudopotentials [12]. Iron d and s electrons were included in the valence, and core electrons were treated using semilocal pseudopotentials. Exchange and correlation energy was treated in the generalized gradient approximation [13]. Comparison with calculations including spin and a higher $E_{\text{cut}}(= 50$ Ry) for model systems (see text) have been performed to ensure convergence in total energy differences. The temperature of the simulation was controlled via a velocity rescaling thermostat and set to 1200 K to correspond to the experimental condition of Ref. [14]. The electrons were kept at 0 K. Simulations were carried out with the GP code (F. Gygi, LLNL).

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[18] The effect of H passivation on the electronic properties of the free catalyst surface was investigated in detail and found to be negligible: electronic structure calculations for one bare Fe_{43} cluster and one with half of the surface atoms passivated by H yield charge densities that differ only in the passivated half of the cluster (H and Fe-H bonds). Electronic states close to the Fermi level are negligibly affected by the passivation, indicating that Fe-C bonds formed during our simulations are mostly unaffected by the artificial H passivation.

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[20] See EPAPS Document No. E-PRLTAO-95-042535 for the molecular dynamics simulation animated sequences. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

[21] We note that the CVD process mimicked by our simulation is substantially different from the arc discharge growth described in Ref. [5]. In that experiment, the discharge causes a mix of carbon and nickel atoms to be evaporated and then rapidly cooled. This leads to the mixing of both species, and a C-saturated liquid Ni droplet is a reasonable starting point to simulate the growth process. In our case, the starting point is the unsaturated metallic particle, as in the experiment of Ref. [4].

[22] Within the GGA approximation, the total energies of Fe_{43} fcc clusters with 1 C atom located in first- or second-shell octahedral sites are, respectively, 1.4 and 2.9 eV larger than that of a surface C atom configuration (C3v symmetry).

[23] Scalar-relativistic pseudopotentials were used for Au. In the case of Fe, our pseudopotential calculations give the following results, compared to experiment. LDA + spin: bcc Fe $a = 5.215$ (5.42 expt) bohr, $u = 2.1$ (2.22 expt) bohr magneton; generalized gradient approximation (GGA)—no spin: bcc Fe $a = 5.48$ bohr ($E_{\text{cut}} = 35$ Ry). With this E_{cut}, interatomic distances are converged to within 0.08 Å, with a deviation of 0.03 Å from the experimental values.