Catalytic Action of Ni Atoms in the Formation of Carbon Nanotubes: A Molecular Dynamics Study

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Catalytic action of Ni atoms in the growth of single-wall carbon nanotubes is investigated using tight-binding molecular dynamics and *ab initio* methods. Our results demonstrate this to be a two step process in which the Ni atom first creates and stabilizes defects in nanotubes. The subsequent incorporation of incoming carbon atoms anneals the Ni-stabilized defects freeing the Ni atom to repeat the catalytic process.

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The recent observation [1] of the dynamic behavior of Ni atoms in graphitic carbon onions [2], by *in situ* atomic resolution electron microscopy, revealed the formation of very interesting C-Ni phases. Most important of these findings is that Ni atoms can take substitutional in-plane positions in graphene layers causing only minimal local distortions to the graphene layer. In particular, it was found that a substitutional Ni atom forms Ni-C bonds of length 0.21 nm with a simultaneous displacement of the Ni atom out of the graphene plane by 0.10 nm. The rest of the graphene lattice was found not to suffer any appreciable distortions. These observations, supported by total energy calculations, and the fact that the substitution of a C atom by a Ni atom in a graphene sheet is energetically not favorable (requiring an energy of 9.9 eV) led Banhart *et al.* [1] to conclude that the Ni atom fills existing vacancies in the graphene sheets when Ni is forced to migrate into carbon onions.

Transition metal catalysts such as Ni are known to play a key role in the production of single-wall carbon nanotubes (SWCN). Microscopic details of their interactions with SWCN are, therefore, expected to shed light on the SWCN growth process. While it is tempting to extrapolate known results of interaction of Ni with graphite to the SWCN case by drawing on the similarities between graphite and SWCN, it should be noted that the curvature can be expected to have nontrivial consequences. Indeed, our recent works have shown that such a simple extrapolation can lead to misleading results for bonding geometries, magnetic moments, and other physical properties [3–6]. A Ni assisted growth mechanism for SWCN has recently been proposed by Lee *et al.* [7] who suggested that the mobile Ni catalyst atoms adsorb at the growing edge of the SWCN where they prevent the formation of carbon pentagons and catalyze the continuous formation of carbon hexagons. This was based on their assumption that SWCN samples were devoid of any remaining metal catalysts and, therefore, the action of Ni is exclusively confined to the tube edge. This is contradicted by recent experiments showing Ni used in the synthesis of SWCN to remain in purified samples even after prolonged treatment in boiling concentrated HNO_3 [8]. Furthermore, chemical analysis, NMR experiments, and high resolution transmission electron microscopy observations suggest an even distribution of small clusters or isolated atoms of these transition metals within the nanotubes [8]. In an earlier work, we have shown the anomalous behavior of conductivity observed in experiment of SWCN to be due to the effects of residual transition metal catalysts residing in close contact with the nanotube walls [9]. Furthermore, we have also shown that contact resistance in SWCN is sensitively dependent on the bonding configurations of transition metal atoms on the nanotube walls [10].

In this Letter, we present results of a detailed theoretical study of the dynamical interaction between the Ni catalyst and SWCN in the presence of additional C atoms with a view towards an understanding of the nanotube growth mechanism. Our calculations are performed using the tight-binding molecular dynamics (TBMD) method [3–5] as well as accurate *ab initio* methods [11]. The details of our TBMD formulation can be found elsewhere [3,12–14]. The TBMD scheme allows us to employ fully symmetry unconstrained optimization for all geometries considered. The TBMD calculations are further complemented by accurate *ab initio* methods [11]. The *ab initio* total energy calculations were performed using the GAUSSIAN 98 program package and includes density functional theory calculations with the three-parameter hybrid functional of Becke using the Lee-Yang-Parr correlation functional [11]. The atomic basis set used is of double zeta quality and includes relativistic effects for heavy atoms.

Our recent works dealing with Ni chemisorption on graphite, C_{60}, and SWCN have demonstrated the profound influence exerted by the curvature of the substrate on Ni bonding properties [3–6]. The curvature effect shows up as a rehybridization of the graphitic-C sp^2 orbitals which in turn bond to the adsorbed Ni *d* orbitals. As shown by us recently [5,6], the nature of the Ni-tube bond depends strongly on the point group symmetry of the adsorption site and the occupancy of the *d* band, the latter exhibiting small spin polarization (as deduced from the small magnetic moment of Ni found on the SWCN). Investigation of the role played by the Ni catalyst in the SWCN must, therefore, take full account of all these effects. In order to understand the Ni catalyzed SWCN growth mechanism we study the behavior of substitutional Ni in the presence of external C atoms in graphite and SWCN using TBMD simulations backed by *ab initio* total energy calculations. The graphite is simulated by a portion of a graphene sheet consisting of 128 carbon atoms. The SWCNs used in our simulations consisted of (5,5) and (10,10) types containing 150 and 320 atoms, respectively. The results obtained are as follows.

(*A*) *Substitutional Ni in a graphene sheet.*—In this simulation we replaced a C atom of a graphene sheet by a Ni atom and allowed the system to relax using the TBMD method [3]. The relaxation resulted in the Ni atom moving slightly outward of the graphene plane with minimal distortions to the rest of the graphene lattice. The Ni-C bonds were found to be 1.63 Å and the C-Ni-C angle 95°–96°. These results are in very good agreement with the experimental and theoretical results of Banhart *et al.* [1]. This should be contrasted with our results for the substitutional Ni impurity in C_{60} [4]. This configuration was found unstable with the Ni atom protruding outward and the C_{59} cage closing underneath, resulting in a stable C_{59}Ni cluster, illustrating the effect of curvature.

(*B*) *Substitutional Ni in a graphene sheet in the presence of an additional C atom.*—After replacing one C atom in a graphene sheet by a Ni atom [as in (A)] we placed one extra C atom above the Ni atom. The TBMD scheme was then used to relax this system. The relaxation resulted in the extra C atom taking the place of Ni, with the released Ni atom chemisorbing below the plane of graphite. Our *ab initio* calculations indicate this process to be energetically very favorable with an energy gain of 21 eV. In the second instance we started the simulation by placing an extra C atom above the center of a hexagon containing one substitutional Ni atom. The outcome of this simulation was identical to the first, showing that, independently of the initial position of the extra C atom, the substitutional Ni atom in the graphene sheet is replaced by a neighboring C atom not belonging to the graphene sheet.

(*C*) *Substitutional Ni in a SWCN.*—We performed TBMD simulations of a substitutional Ni atom in a (5,5) as well as a (10,10) SWCN tube. In both cases the relaxation resulted in the Ni atom moving into the interior of the nanotube leaving a C vacancy on the wall with the distortions of the SWCN confined mainly to the neighbors of the vacancy (Fig. 1). It is worth noting that in the relaxed position the Ni atom binds to all the C atoms surrounding the C vacancy created by Ni with Ni-C bond lengths ranging from 2.03 to 2.08 Å. Thus, the presence of the Ni atom appears to stabilize the C vacancy in the SWCN.

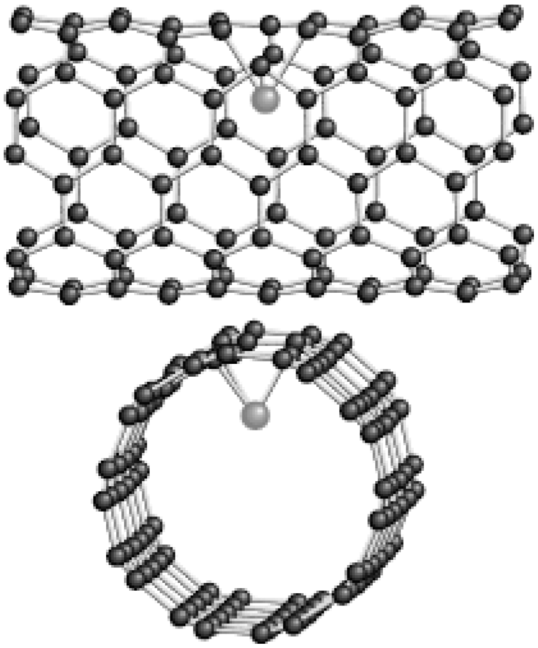

FIG. 1. Molecular dynamics simulation of a substitutional Ni atom in a (5,5) nanotube. The relaxation resulted in the Ni atom moving into the interior of the nanotube leaving a C vacancy on the wall with the distortions of of the SWCN confined mainly to the neighbors of the vacancy.

More accurate quantitative results on the stability of the relaxed configuration can be obtained by performing *ab initio* [11] calculations. We calculate the total energy of the system using *ab initio* methods starting from the relaxed Ni position shown in Fig. 1 and then by moving the Ni atom radially outward to an exterior position in small increments. Figure 2 shows a plot of the total energy obtained at the various Ni positions. From this it is clear that the Ni atom is, in fact, more stable either outside or inside the tube, while its substitutional position is a transition state. The asymmetry seen in the barrier between the inside and the outside Ni sites with respect to the tube wall is due to the different curvature effect on each of these sites. This asymmetry, however, will dictate the way the Ni atom will move when it finds itself near the tube wall. We have further performed high temperature simulations to check the stability of the vacancy in the nanotube with and without the presence of Ni. We find both configurations to be stable at $T \approx 1000$ K in the absence of external carbon atoms. However, the Ni stabilized vacancy is more stable on account of the saturation of carbon dangling bonds.

Two additional TBMD simulations involving substitutional Ni atoms in a SWCN were also carried out. In the first of these, we replaced a C atom at the open end of a (4,4) tube by a Ni atom. In this case, the Ni atom is at the exterior carbon ring. Upon relaxation, the Ni atom retained

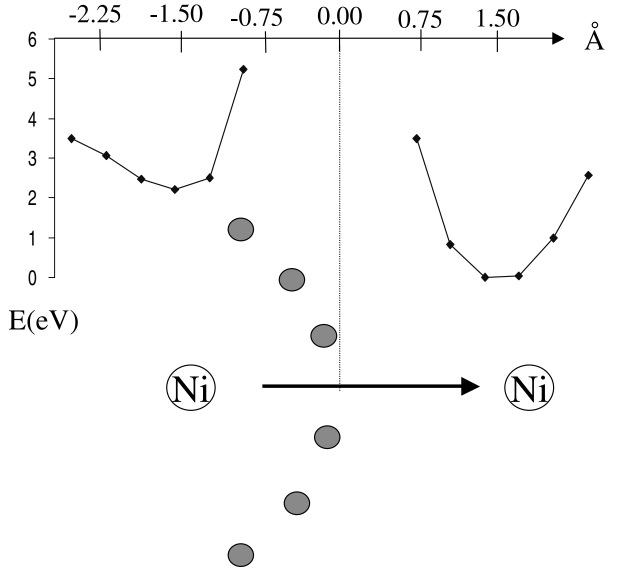

FIG. 2. *Ab initio* total energy of the system at various Ni positions starting from the relaxed position shown in Fig. 1 and then by moving the Ni atom radially outward to an exterior position in small increments.

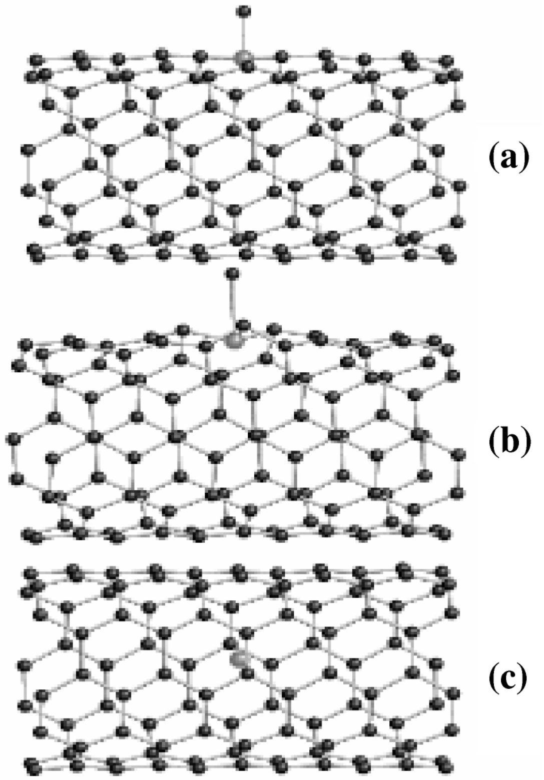

FIG. 3. (a) Starting configuration, (b) intermediate stage and, (c) final configuration of the TBMD simulations of a (5,5) carbon nanotube containing a substitutional Ni atom in the presence of an incoming C atom within bonding distance of Ni. In the final configuration the Ni atom has been replaced by the incoming C atom while the Ni atom is left encapsulated inside the tube but no longer bonded to any of the C atoms belonging to the nanotube.

its initial position while inflicting considerable distortions at the open tube end. In the second simulation, we replaced a carbon atom, located on the second C ring from the open end of the (4,4) tube by a Ni atom. Interestingly, the TBMD relaxation caused the Ni atom to move to an exterior position, i.e., form a part of the exterior carbon ring. The Ni-C bond lengths in the relaxed configuration range from 1.91 to 2.01 Å.

(*D*) *Substitutional Ni atom in a SWCN in the presence of an additional C atom.*—Simulations described in (C) were repeated by including an additional C atom within bonding distance of the substitutional Ni atom in a (5,5) tube. The starting configuration is shown in Fig. 3a. Upon relaxation the substitutional Ni atom was replaced by the exterior C atom, while the Ni atom broke free and was left encapsulated inside the tube with no bonding to any of the C atoms. The final relaxed geometry showing complete healing of all distortions caused by Ni is shown in Fig. 3c, while the intermediate stage of the simulation is illustrated in Fig. 3b. A careful observation of the relaxation process suggests that a C vacancy is first created by a substitutional Ni atom; the vacancy then draws into it an external C atom in the atmosphere, annealing the vacancy and freeing the Ni atom. We further performed *ab initio* total energy calculations for the system starting from the configuration in Fig. 3a and moving the Ni-C dimer radially inward along the path taken by the Ni-C dimer in the TBMD simulations. The total energy of the system along this path, shown in Fig. 4, demonstrates that the substitution of a Ni atom on the wall of the carbon nanotube in the presence of an extra C atom is not energetically favorable and that the stable sites are separated by a considerable energy barrier (10.5 eV).

These results clearly demonstrate a contrasting dynamic behavior of the substitutional Ni atoms in graphite and in SWCNs. In particular, they show that, contrary to their behavior in graphite, substitutional Ni atoms are not stable on the SWCNs. Furthermore, our dynamical simulation results allow us to propose a reasonable explanation for the catalytic role of the Ni atoms in the growth process of carbon nanotubes as follows.

(i) The Ni atoms act as stabilizing agents of the structural defects created in SWCN during the growth process. When other carbon atoms in the atmosphere come within bonding distance of such a Ni-stabilized defect, the defect is annealed while the freed Ni atom diffuses along the length of the tube either outside or inside.

(ii) At the end of the tube, the substitutional Ni atom can remain stable, forming part of the hexagonal ring, although with considerable distortions. However, when new hexagons start to form by the incorporation of additional carbon atoms in the atmosphere, the Ni atom exchanges its position with an incoming carbon atom and resets itself by occupying a substitutional position on an exterior ring. Our *ab initio* total energy calculations support the TBMD

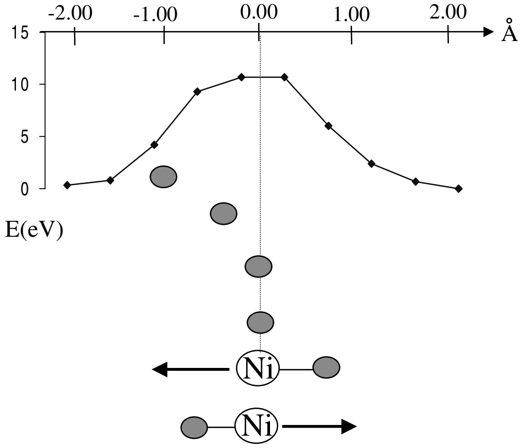

FIG. 4. Plot of *ab initio* total energy for the system starting from the configuration in Fig. 3a and moving the Ni-C dimer radially inward along the path taken by the Ni-C dimer in the TBMD simulations.

results and show that this process is energetically very favorable with an exothermic release of 7.25 eV.

Our mechanism is in striking contrast to that proposed by Lee *et al.* [7] where the primary role of Ni, acting alone, is to prevent tube closure by inhibiting the formation of pentagons. Furthermore, according to Ref. [7], the action of Ni is exclusively confined to the tube edge. In the present work we have shown that the Ni atom cannot act on its own; its action is mediated by existing or created (by the Ni) structural defects. The presence of the Ni atom is necessary either to prevent these defects from spreading across the tube or to anneal them by a swapping process.

Our dynamical simulations also rule out the "scooting" mechanism proposed in Ref. [7] in which the Ni atom goes around the tube edge. Our *ab initio* calculations yield an energy barrier of 1.3 eV for Ni hopping from one armchair edge to another. This value for the barrier height is larger by 0.35 eV than the value found by Lee *et al.* (as deduced from Fig. 1 of Ref. [7]). Because of the exponential dependence of the diffusion coefficient on the barrier height, our results correspond (using the assumptions of Lee *et al.* [7]) to a much smaller ($\approx 1-2$ orders of magnitude) scooting rate of Ni around the tube edge. Our simulations, instead, favor the Ni atom acting initially as a defect stabilizer and subsequently diffusing (by a position-exchange mechanism described earlier) to a substitutional position on an exterior ring. It should be noted that in Ref. [7] the growing edge of the carbon nanotube was modeled by a small graphene flake containing only 20–30 atoms. Our TBMD simulations in conjunction with *ab initio* total energy calculations have shown that such a simple interpolation of the results for Ni interaction with graphite to predict similar properties for Ni with nanotube can lead to qualitatively different results [3–5].

The encapsulation tendency we find in the case of substitutional Ni in the presence of an incoming C atom is supported by the recent experimental work reported in Ref. [8] where encapsulation of Ni/Co is suggested as the most probable processes taking place during the tube growth. Our simulations, thus, give a detailed description of the possible swapping processes involved in the Ni assisted catalytic growth of nanotubes.

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