Ab initio study of the effect of nitrogen on carbon nanotube growth

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Abstract
The energetics and kinetics of carbon nanotube growth are studied using an
ab initio method. Specifically, the role of the nitrogen atom is analysed in
detail for various pathways to the growth of the nanotube edge. The energy
barriers are estimated by identifying transition states and it is found that the
growth rate of a zigzag-type edge is significantly enhanced. The underlying
physical mechanism is explained based on the electronic structure of nitrogen
atoms embedded in the carbon networks.

1. Introduction

Carbon nanotubes (CNTs) have been regarded as one of the
strong candidates for various industrial applications ranging
from flat panel display to energy storage materials [1, 2].
For these applications, it would be a prerequisite to control
the structure and chemical composition of the CNTs in a
systematic manner. Investigations of the growth procedure
in detail are thus very important. Without understanding the
growth mechanism of CNTs, it would be difficult to predict
and manipulate the growth structure of CNTs. For example,
the chirality of CNTs, which is essential in implementing CNT
devices, can be controlled only when the growth procedure
is fully understood [3]. However, the growth mechanism of
CNTs is yet to be clarified [4].

One should also note that the composition of CNTs can
be varied with the deposition conditions. After the initial
reports on nitrogen doping in nanotubes [5], many experiments
using the CVD process showed that a nitrogen environment
in the growth stage enhanced the CNT, growth resulting
in vertically aligned CNTs [6–9]. High-resolution electron
energy loss spectra (EELS) of the CNTs revealed that nitrogen
atoms are incorporated in the nanotube wall and cap when
activated nitrogen atoms, decomposed from N_2 or NH_3, exist

in the deposition environment [10, 11]. Since the chemical
composition affects the physical and chemical properties of
CNTs, the composition variation of CNTs should be carefully
considered.

Recently, Kim *et al* reported experimental evidence that
the enhanced growth of CNTs in the activated nitrogen
environment is closely related to the nitrogen incorporation to
the CNT wall or cap [8]. Even if the previous work definitely
showed an intimate relationship between the CNT growth rate
and the nitrogen incorporation, the current understanding on
the role of nitrogen atoms in CNT growth is rather qualitative.
In the present work, we investigate theoretically the role of
nitrogen in CNT growth by using an *ab initio* calculation based
on the density functional theory. Transition state calculations
were carried out on each step of the growth by using the
computation package of DMol^3 [10]. The present calculation
shows that the nitrogen incorporation reduced the kinetic
barrier of zigzag edge growth. In particular, when nitrogen
is located on the growth edge, the kinetic barrier for the growth
can be reduced to zero, depending on the position of the
incorporated nitrogen.

2. Computational approach

We use the computational package of DMol^3 throughout
this work [12]. The wavefunctions are expanded with

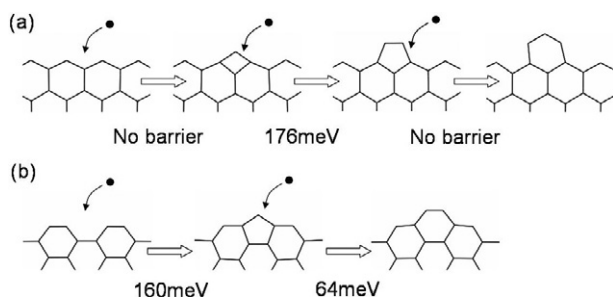[4] Author to whom any correspondence should be addressed.

Figure 1. The sequences towards creating one hexagon cell on (a) a zigzag edge and (b) an armchair edge of pure carbon systems. The small dots indicate carbon atoms added sequentially. The computed reaction barriers are also shown below.

double-zeta polarization basis and the atomic coordinates are relaxed until the Hellmann–Feynman forces are less than 0.004 Ha (Hartree) $Å^{-1}$ and the energy change between relaxation steps is less than 2×10^{-5} Ha. For the description of exchange and correlation energy of the electron gas, we employ the generalized gradient approximation [13, 14]. In this work, we consider a possibility that the nitrogen atom assists the formation of the growth precursor of CNTs and provides an easy nucleation path of hexagons at the growth front. For simplicity, we study the growth kinetics of graphite flakes made of 50–60 atoms assumed to mimic the open edges of typical CNTs [15] (see figure 1). Even though the simulation of full processes of the CNT growth has recently been reported [16], it is still computationally very demanding. Therefore, we assume that the growth is reasonably simulated as adding foreign carbon atoms sequentially at the growth front. The dangling bonds outside the growing region are passivated by hydrogen atoms. In the planar hexagonal network, there are two kinds of front edge: zigzag and armchair edges. In general, the growth front of the CNT is mixed with both types of edges and the growth kinetics of both cases should be taken into account in the actual situation. We remark on the use of the flat graphene models. By the cluster design calculation [17], we examine the strain energies of CNTs with radii from 4 to 200 Å. The computational results show that the excess strain energy is essentially zero for a radius bigger than 35 Å. Since the typical radii of the nitrogen-doped CNTs are in the range 150–200 Å, i.e., multi-walled, the nanotubes can be considered as a strain-free structure such as a flat graphene model.

The kinetic energy barrier (E_b) for each reaction step is obtained by locating the transition state. We employ the LST (linear synchronous transit)/QST (quadratic synchronous transit) method [18, 19] implemented into DMol^3. In the LST approach a series of single point energy calculations is performed on a set of linearly interpolated structures between a given reactant and product. The maximum energy structure along this path provides an initial guess in a local relaxation orthogonal to the LST path, which is then used as an intermediate to define a QST pathway. In the QST model, the energy maximum along the quadratic path is predicted.

3. Results and discussions

We begin with cases where the nitrogen atom is absent. Figure 1 shows the sequential attachment of carbon atoms on

each type of front edge. Three carbon atoms are required on the zigzag edge to form another hexagon ring, which proceeds through three consecutive reaction steps in our model. On the armchair edge, on the other hand, the addition of a hexagon ring involves two reaction steps. The computed energy barriers for each reaction step are also shown in figure 1. It is interesting that the energy barriers are nonzero in several steps in spite of the high chemical reactivity of carbon atoms added at the edge. In the formation of a hexagon on the zigzag edge shown in figure 1(a), only the transition from tetragon to pentagon requires E_b of 176 meV. We find that the tetragonal ring on zigzag edge results in substantial curvatures around the tetragon, indicating that the subsequent reactions are under the influence of the induced curvature effects. During the transition from pentagon to hexagon, a foreign carbon atom can be attached either at the side or at the top of the pentagon. The computed energy barriers are 0 and 43 meV, respectively, and so the reaction will proceed through the former configuration. This is related to different strengths of the C–C bond at the top and side of pentagon where triple and double bonds are formed at the top and the side, respectively. On the armchair edge shown in figure 1(b), the pentagon formation requires E_b of 160 meV, and the transition from pentagon to hexagon also requires E_b of 64 meV. Based upon these data, it can be inferred that the growth on the armchair edge will be slightly faster considering the usual growth temperatures of $\geqslant 600\,°C$. We note that after nucleation of one protruding hexagon on the zigzag edge, the horizontal addition of the hexagon is effectively identical to that of the armchair edge in figure 1(b).

Now we consider cases where a nitrogen atom is involved during the CNT growth. Figures 2(a) and (b) show two ways of how a nitrogen atom is added at the armchair edge. When a nitrogen atom is introduced in the pentagon–hexagon transition (figure 2(a)), the energy barrier increases to 137 meV, up from 64 meV for pure carbon edges (see figure 1(b)). In the other case, the nitrogen atom is used for making a pentagon (figure 2(b)) and the energy barrier is as high as 303 meV, and the following carbon attachment also has a very high energy barrier of 5455 meV. This can be ascribed to the short and strong C–N bond compared to C–C bond. Since the two reaction paths are mutually exclusive, the former pathway would be preferred. Possible reaction paths on the zigzag edge are shown in figures 2(c)–(e). The energy barrier is slightly lowered in figures 2(c) and (d) while it is almost unchanged in figure 2(e). As a result, the presence of a nitrogen atom will slightly enhance the nucleation rate of the hexagon on the zigzag edge.

Next, we study how the nitrogen atom introduced into the carbon network affects the subsequent reaction. Depending on the local configuration around the nitrogen atom, one can find two disparate locations in which the nitrogen atom sits. One is the valley site, a concave-shaped position between hexagon rings (figures 3(a) and (c)) and the other is the top site or vertex position of a hexagon (figures 3(b) and (d)). On the armchair edge, the pentagon formation has the maximum energy barriers regardless of the nitrogen position: 152 meV when nitrogen is at the valley site or 179 meV at the top site (figures 3(a) and (b)). Figures 3(c) and (d) show the schematic growth paths of a zigzag edge in the presence of nitrogen. When the nitrogen is placed at the valley site,
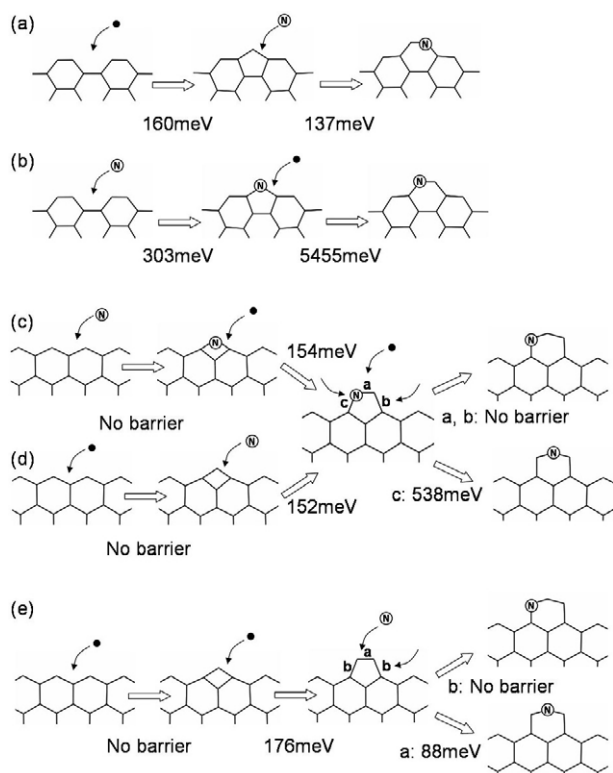
Figure 2. Schematic diagrams for nitrogen incorporation during the hexagon formation. Armchair edges are shown in (a) and (b) and zigzag edges are shown in (c)–(e).

Figure 3. Possible reaction paths for carbon incorporation when a nitrogen atom is present in nearby locations. In (a) and (c), the nitrogen atom is embedded in the valley site while it is exposed at the top site in (b) and (d).

Figure 4. The electronic charge density of the configuration in a dashed box in figure 3(d) where the energy barrier is very low. Note that the charge density along one of the C–N bonds is completely depleted and this will be easily broken by incoming carbon atoms.

tetragon formation occurs spontaneously without an energy barrier. However, the tetragon–pentagon transition has a large reaction barrier of 333 meV, meaning that the nitrogen greatly stabilizes the tetragonal defects. Because of the large barrier for completing the hexagonal shape, the further growth of graphitic edges in this area is likely to start after adjacent hexagons are formed and this will result in defective CNTs by creating a large population of topological defects on the CNT wall. Once a pentagon is formed with nitrogen at the valley site, the transition to the hexagonal ring has no reaction barrier. However, the overall kinetic rate of this reaction sequence is controlled by the pentagon formation with a reaction barrier of 333 meV. The most striking feature is found in figure 3(d) with a nitrogen atom located initially on the top site of the zigzag edge. It is found that energy barriers for all steps toward hexagon addition completely disappear. This indicates that the nucleation of a hexagon on the zigzag-shaped edge is greatly accelerated, only to be limited by the energy barrier for forming an armchair-type edge. This result implies that armchair growth is the rate control step of CNT growth. This is in comparison with the effect of boron atoms, which enhances the growth of zigzag nanotubes [20].

To understand the underlying physics of the barrier-free path in figure 3(d), we plot the distribution of electronic densities of a boxed middle step in figure 4. The stable lone pair originating from the nitrogen atom is shown as large electronic densities around the nitrogen atom. Consequently, the atomic bonding between the nitrogen atom and the carbon atom above has almost vanished. The incoming carbon atom will be easily bound to this carbon atom because of the
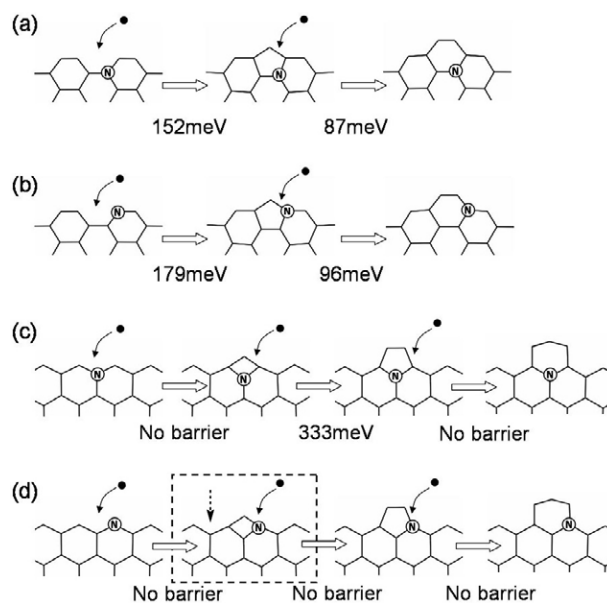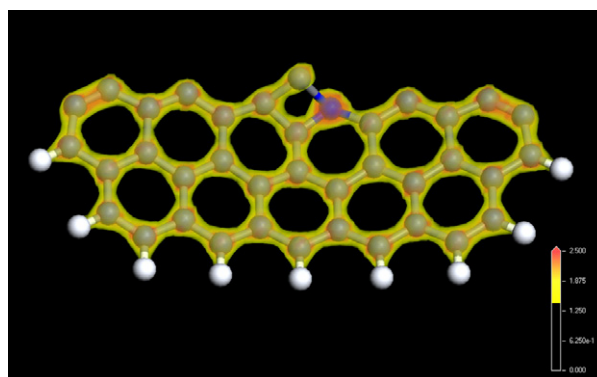
extremely reactive dangling bond, resulting in barrier-free addition. On the other hand, a different explanation applies to the zero barrier reaction occurring during the tetragon or hexagon formation in figure 3(c). These are essentially the same as those in the pure carbon edge where the evolution from to tetragon or hexagon takes place without a barrier (figure 1(a)). Tetragon formation is highly preferred due to the high chemical activity of the zigzag edge. In the case of pentagon to hexagon transition, the C–C bonding at the top and side of pentagon is substantially weaker than those of, for example, C–C bonding of a hexagon at the armchair edge (see figure 1(b)) with a similar shape (the bond lengths are 0.02–0.1 Å longer). This facilitates the incorporation of a carbon atom with negligible energy barrier.

In figure 3(d), if a carbon atom is added at the C–C bonding indicated by the dashed arrow, this also leads to zero energy barrier with the adjacent C–N bonding completely

broken. This is an interesting result because the remaining nitrogen atom forms a bonding with two carbon atoms below, a signature of pyridine-like bonding [21]. Since the nitrogen atom in this configuration is saturated with chemical bonding, there is a good chance that further reactions with incoming carbon atoms will form a pyridine-like bonding.

4. Conclusion

The role of nitrogen incorporation in CNT growth was investigated by *ab initio* calculations. The nitrogen incorporation mainly changes the rate-limiting step of the CNT growth from zigzag edge growth to an armchair one by considerably reducing the energy barrier of the zigzag edge growth. This also indicates that the growth rate of the zigzag edge and armchair edge can be controlled by introducing foreign atoms with different chemical valence. This could be used in controlling the chirality or electronic properties of CNTs at the growth stage, rather than post-processing techniques [22, 23]. The kinetic Monte Carlo simulation based upon the parameters obtained in this work will be able to provide a more complete picture of nanotube growth under the effect of a nitrogen environment and this will be done in a future study.

Acknowledgments

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