A molecular dynamics study of the graphitization ability of transition metals for catalysis of carbon nanotube growth via chemical vapor deposition

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A B S T R A C T

The graphitization ability of several transition metals used as catalysts for carbon nanotube growth via chemical vapor deposition has been investigated via classical molecular dynamics simulation on planar crystalline metal surfaces and metal nanoclusters. Open-packed facets are shown to be a good template for reconstructing graphene structure since they exhibit some degree of epitaxy with hexagonal carbon network. Moreover, the interaction energy between an iron cluster and graphene sheet was found to be higher than for clusters comprising cobalt or nickel, since the high energy of graphene due to induced defects is stabilized by interaction with surfaces of iron cluster.

1. Introduction

The growth mechanisms [1] of single-wall carbon nanotubes (SWCNTs) have been widely studied since they were first brought to the attention of the scientific community at large [2]. With the development of catalytic chemical vapor deposition (CCVD) techniques [3–6] as a promising synthesis method for both single and multi-wall tubes, growth models to describe metal-catalyzed growth have been widely discussed [1,7]. In 2003, Shibuta and Maruyama [8] first reported classical molecular dynamics (MD) simulations showing a nanotube-cap growth process occurring on a metal cluster, which have also been observed since by a number of other groups [9–15]. Combined with the support of in situ observations [16], these numerical simulations have given rise to a broad consensus that the initial cap structure of the carbon nanotube is nucleated by a transition metal catalyst nanocluster, followed by subsequent longitudinal growth either from tip or root of the tube. Furthermore, the effect of the substrate on CNT growth has also been investigated by classical MD simulation [17,18]. Recently, not only the initial cap formation process, but also the subsequent longitudinal growth process has been captured by the present authors using a multi-scale modelling approach [19,20].

One of the most significant unresolved issues related to the nanotube growth is to understand the factors determining the chirality of grown CNTs. Several previous reports have shown that epitaxy between the graphene sheet and crystallographic facets of catalytic metal clusters may be important in determining the chirality of the CNTs [21,22]. Moreover, the surface crystallographic orientation of the catalytic metal clusters is sensitive to

their bulk structural configuration [23], which is in turn related to the phase of the cluster. Since the phase of the cluster is difficult to define clearly, the effect of size on the phase of the nanoparticle has been widely studied [23–28]. For example, Harutyunyan et al. [24] examined the phases of cobalt nanoparticles during CNT growth by calorimetric measurements and concluded that the liquid phase is most favorable for the growth of SWCNTs. Depression of the melting point of nanoparticles due to the Gibbs–Thomson effect was confirmed by MD simulation of phase transition process of metal nanoparticles [25,26]. Moreover, discussion of the Fe–C phase diagram as a function of the nanoparticle size on the basis of MD simulation [27] and ab initio calculations [28] have demonstrated that formation of cementite arrests the formation process of nanotubes due to its different activity and diffusion properties. Although the stability of the graphene in the metal cluster has been discussed at length in the above studies, the catalytic ability of the transition metals is still under debate. From previous experimental work, it is known that the best catalysts for SWCNT growth have a high graphitization ability, low solubility for carbon and stable crystallographic orientation on graphite [29]. The graphitization ability, which is defined as the ability of a catalytic surface to stabilize the formation of a defective graphene sheet so that it can anneal to make a perfect sheet, has not yet been the explicit focus of any theoretical studies to date. Therefore, the graphitization ability of several transition metals commonly used as catalysts for carbon nanotube growth has been investigated here via classical molecular dynamics simulation. After briefly summarizing the simulation methodology in Section 2, the remainder of the paper is structured as follows: first, the stability of the graphene sheet on the surface of the bulk metal is examined in Section 3.1; then, the stability and the interaction energy between graphene sheet and metal cluster are discussed in Section 3.2.

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2. Simulation methodology

A classical MD method was used to study the graphitization ability of transition metals for catalysis of carbon nanotube growth. A Brenner potential [30] in its simplified form [31] was used to describe covalent bonding between carbon atoms. A bond-order type potential [22], which was constructed for transition metal carbide cluster, was used to describe metal–metal and metal–carbon interactions in which the bonding energy between atom $i$ and $j$ is expressed as:

$$E_{ij} = V_A - B^* V_H$$

(1)

$$V_B = f(r_{ij}) \frac{D_e}{S-1} \exp \left\{ -\beta \sqrt{2S(r_{ij} - R_e)} \right\}$$

(2)

$$V_A = f(r_{ij}) \frac{D_S}{S-1} \exp \left\{ -\beta \sqrt{2S(r_{ij} - R_e)} \right\}$$

(3)

where $r_{ij}$ is the distance between atom $i$ and $j$, $D_e$ is the binding energy, $R_e$ is the equilibrium bond energy and $f$ is the cut-off function, respectively. The potential parameters $S$ and $\beta$ determine the shape of the Morse-type repulsive term, $V_B$ and attractive term $V_A$. For carbon–carbon interactions, the additional term $B^*$, which describes the many-body effect, is expressed as:

$$B^* = \frac{B_B + B_g}{2}$$

(5)

$$B_B = 1 + \sum_{k\neq j} \left\{ \frac{G_C(\theta_{ijk}) f(r_{ik})}{2} \right\}$$

(6)

$$G_C(\theta) = a_0 \left( 1 + \frac{c_0^2}{d_0^2} \frac{c_0^2}{d_0^2} + (1 + \cos \theta) \right)$$

(7)

where $\theta_{ijk}$ is the angle made by a bonded triplet of atoms $i$, $j$ and $k$. For metal–carbon interactions, the additional term $B^*$ is expressed as:

$$B^* = (1 + b(N^C - 1)) v$$

(8)

$$N^C = 1 + \sum_{\text{carbon } k \neq i} f(r_{ik})$$

(9)

where $N^C$ is the number of carbon atoms coordinating a metal atom $i$. For metal–metal interactions, the binding energy and the equilibrium bond length are expressed as a function of the metal coordination number instead of using the additional term $B^*$:

$$D_g = D_{g1} + D_{g2} \exp\left\{ -\frac{C_0}{N^g} \right\}$$

(10)

$$R_e = R_{g1} - R_{g2} \exp\left\{ -\frac{C_0}{N^g} \right\}$$

(11)

$$N^M = \frac{1}{2} + \sum_{\text{metal } k \neq i} f(r_{ik})$$

(12)

where $N^M$ is the metal coordination number of a metal atom $i$. Parameter sets derived for these potential functions are given in Ref. [22] (for the metal–carbon and metal–metal interactions) and Ref. [30] (for carbon–carbon interactions). The interaction between metal atoms in the cluster and the planar substrate (i.e. the bottom boundary of the calculation cell) was expressed using a one-dimensionally averaged Lennard-Jones (1DLJ) potential [17]:

$$F(z) = D_1 \left\{ \frac{1}{5} \left( \frac{z}{d} \right)^{10} - \frac{1}{2} \left( \frac{z}{d_0} \right)^{12} \right\}$$

(14)

where $z$ is the Cartesian coordinate normal to the substrate plane. This potential function represents the integrated interaction between a metal atom in the cluster and all atoms on the substrate calculated using a standard 12-6 Lennard-Jones potential function. The parameter $\sigma$ was set to 3.23 Å, as determined from the van der Waals radius of a Si atom [17]. The parameter $D_1$ was varied from 0.5 to 1.25 eV at 0.25 eV intervals in order to describe the variable affinity of the metal cluster for the substrate. The velocity Verlet method was used to integrate the classical equations of motion with a time step of 0.5 fs, and a Berendsen thermostat [32] was used for temperature control with a relaxation time of 0.17 ps. Schematic images of the simulation cell for the calculation of the stability of the graphene on the bulk surface and the interaction between the graphene and metal cluster are shown in Fig. 1, with the crystal surface or substrate lying perpendicular to $z$ direction and periodic boundary conditions applied in the $x$ and $y$ directions.

3. Results and discussion

3.1. Stability of the graphene on the surface of the bulk metal

Before considering nanoparticles, which generally exhibit a variety of crystalline facets, the stability of graphene on various surfaces of the bulk crystalline metals was first examined. A schematic image of calculation process is shown in Fig. 1a. Three layers of the Ni(111)$_\text{fcc}$, Co(0001)$_\text{hcp}$ and Fe(001)$_\text{bcc}$ surfaces were prepared at the base of the cubic cell, with the close-packed surfaces comprising of 672 atoms, and the cubic-packed surfaces consisting of 484 atoms, respectively. A defect-free graphene sheet con-

![Fig. 1. Schematic images of the simulation methodology for calculating: (a) stability of the graphene on the bulk surface and (b) interaction between the graphene and metal cluster.](image-url)
sisting of 640 carbon atoms (periodic in x and y directions) was then deposited with a kinetic energy of 2.48 eV atom \(^{-1}\) onto the Ni(111)\(_{fcc}\), Co(0001)\(_{hcp}\) and Fe(001)\(_{bcc}\) surfaces. The system was then annealed on the metal surface at 1500 K, with the metal atoms being fixed (at 0 K) during annealing. Fig. 2 shows selected snapshots of annealing process of the graphene sheet onto the metal surface. After some initial bond breakage due to kinetic energy of impact with the metal surface, the carbon atoms began to migrate on the metal surface. In the case of the close-packed Ni(111)\(_{fcc}\) and Co(0001)\(_{hcp}\) surfaces, the hexagonal graphene network was rapidly reconstructed. However, as shown in Fig. 2c, the graphene structure was not readily recovered on the cubic Fe(001)\(_{bcc}\) surface, since there is little epitaxy with the hexagonal carbon network compared to the two-dimensional closed-packed facets.

Fig. 3 shows time series of the potential energies of the graphene sheet per carbon atom and that of the crystalline metal per metal atom. After impact of the graphene sheet onto the metal surface, the potential energy of the carbon and metal atoms decreased due to the interaction between them. In this case, the

![Fig. 2. Snapshots of annealing process of the graphene sheet onto the Ni(111)\(_{fcc}\), Co(0001)\(_{hcp}\) and Fe(001)\(_{bcc}\) surface. White, red, orange, green and purple spheres represent carbon atoms with 0, 1, 2, 3 and 4 carbon-covalent bonds, respectively. The abscissa shows the time after impact of the graphene to the metal surface. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 3. Time series of the potential energies of the graphene sheet per carbon atom and that of the crystalline metal surfaces: (a) Ni(111)\(_{fcc}\), (b) Co(0001)\(_{hcp}\) and (c) Fe(001)\(_{bcc}\) per metal atom during annealing process.](image)
potential energy of the carbon atom takes into account both carbon–carbon and carbon–metal interaction. However, by considering the potential energy derived from the carbon–carbon interaction only, the potential energy increased from $-7.147$ to $-6.811 \text{ eV atom}^{-1}$ for nickel, $-6.108 \text{ eV atom}^{-1}$ for cobalt and $-4.905 \text{ eV atom}^{-1}$ for iron, respectively. In the case of the iron, the dramatic increase in energy derived from the carbon–carbon interaction is due to the disruption of the hexagonal graphene network. The interaction energy of the metal surface and the annealed graphene sheet on the surface was calculated from the energy difference between the total energy of the crystalline metal and the annealed graphene sheet and the sum of the energies of the individual crystalline metal and graphene sheet. Then, the energy difference was divided by the area of the graphene sheet, $1641.4 \text{ Å}^2$, to estimate the interaction energy per unit area. The interaction energies were $1.489 \text{ eV Å}^{-2}$ for nickel, $2.437 \text{ eV Å}^{-2}$ for cobalt and $3.461 \text{ eV Å}^{-2}$ for iron, respectively. The high interaction energy of the annealed graphene sheet and crystalline metal is due to defects stabilized by interaction with the surface of the crystalline metal.

For comparison with the above results, the interaction energy of a perfect graphene sheet and the various crystalline metal surfaces was also calculated. Fig. 4 shows the energy gain of a perfect graphene sheet per carbon atom and crystalline metal surface per metal atom as a function of the separation between them. All energy curves show a minimum around a distance of about 1.5 Å. The interaction energy per unit area was estimated from the minimum value of the energy gain as, $1.298 \text{ eV Å}^{-2}$ for nickel, $1.801 \text{ eV Å}^{-2}$ for cobalt and $1.304 \text{ eV Å}^{-2}$ for iron, respectively. The interaction energy for cobalt was larger than the others, although both Ni(111)$_\text{fcc}$ and Co(0001)$_\text{hcp}$ surfaces are crystallographically equivalent. Moreover, there is little difference between the interaction energy for nickel and iron, although the process of reconstructing the graphene sheet on either surface is quite different as evidenced by the large difference in interaction energies for a defective sheet found above. Thus, in order to examine in more detail the nature of epitaxy between the two-dimensional closed-packed facets and the graphene sheet, the potential energy surface felt by carbon atoms near the metal surface was constructed.

Fig. 5 shows potential energy surfaces felt by a carbon atom from the Ni(111)$_\text{fcc}$ and Fe(001)$_\text{bcc}$ surface at the distance of 1 Å from the metal surface. The potential energy surface was calculated using the same interatomic potential used above. In the case of the Ni(111)$_\text{fcc}$ surface, the potential minimum arises at the center of a triangle made by three neighboring atoms. The surrounding

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![Fig. 4](image-url)  
Fig. 4. Energy gains of the perfect graphene sheet per carbon atom and crystalline metal surfaces: (a) Ni(111)$_\text{fcc}$, (b) Co(0001)$_\text{hcp}$ and (c) Fe(001)$_\text{bcc}$ per metal atom as a function of the distance between the graphene and metal surface.

![Fig. 5](image-url)  
Fig. 5. Potential energy surface felt by a carbon atom from the (a) Ni(111)$_\text{fcc}$ and (b) Fe(001)$_\text{bcc}$ surface at the distance of 1 Å from the metal surface. Contour lines were drawn with an energy interval of 1 eV for nickel and 2 eV for iron, respectively. The dotted lines indicate distances between the nearest energy-minimum points for nickel surface.
potential minima are distributed in a hexagonal pattern, as shown by the dotted lines in the Fig. 5a. The in-plane nearest neighbor distance for Ni(111)$_{fcc}$ is 2.49 Å at room temperature [33] and so the distance between centers of triangles is approximately 1.44 Å, which is close to the equilibrium bond length of a carbon–carbon bond in graphene. Hence, the Ni(111)$_{fcc}$ surface has the potential to act as a good template for the hexagonal carbon network, which is why the graphene sheet was rapidly reconstructed on the Ni(111)$_{fcc}$ and Co(0001)$_{hcp}$ surfaces. This observation is in agreement with an experimental report by Yudasaka et al. [29] that X-ray-diffraction of graphite deposited on nickel shows that Ni(111)$_{fcc}$ lies reproducibly parallel to the graphite surface. Moreover, Amara et al. [34] have performed a tight-binding grand canonical Monte Carlo simulations which revealed that the carbon nanostructure on the Ni(111)$_{fcc}$ surface varies between chains, a detached sp$^2$ layer and amorphous, depending on the chemical potential of the carbon. This implies that the graphene sheet can be formed in the presence of carbon atoms of the appropriate concentration on the Ni(111)$_{fcc}$ surface. On the other hand, as shown in Fig. 5b, the Fe(001)$_{bcc}$ surface has potential minima distributed in reticular pattern without hexagonal symmetry. Hence, the graphene structure was not readily recovered on the Fe(001)$_{bcc}$ surface since this surface does not possess good epitaxy with graphene sheet.

3.2. Interaction energy between graphene and metal cluster

Having investigated planar surfaces, the interaction between graphene and transition metal nanoclusters was examined based on our previous study [19]. At first, initially fcc nanoparticles of nickel, cobalt and iron with 256, 500 and 864 atoms were annealed for 100 ps at 1500 K, resulting in a series of disordered configurations. Ten different configurations were extracted at every 10 ps during annealing for each metal. Then, the clusters obtained were annealed on a smooth planar substrate, represented as described in Section 2, for 10 ps at 1500 K. The binding energy of the 1DLJ potential was varied from 0.5 to 1.5 eV in 0.05 eV increments. Hence, 630 different configurations were obtained for each metal. The contact angle of the cluster to the substrate was estimated by assuming that the clusters are approximately spherical [19]. Fig. 6a shows the plots of the contact angle as a function of the binding energy of the 1DLJ potential. A larger binding energy led to an increased wetting of the substrate by the cluster, and hence the contact angle is negatively correlated with the binding energy of the 1DLJ potential. The data were fitted to the linear function by least-squares regression analysis. The gradients of the fitted functions for clusters with 256, 500 and 864 atoms are $-51.64$, $-36.54$ and $-29.66$ deg eV$^{-1}$ for nickel, $-49.44$, $-34.38$ and $-26.19$ deg eV$^{-1}$ for cobalt, and $-45.95$, $-35.69$ and $-26.19$ deg eV$^{-1}$ for iron, respectively. The gradient increased with decreasing cluster size, which is consistent with the results from our previous study [19]. Among the three metals considered here, the gradient for the nickel cluster was largest and that for the iron cluster was smallest.

Having obtained a series of structures for substrate-supported catalyst particles, the interaction energy between a graphene sheet and adsorbed metal cluster was examined. In order to do this, each of the clusters obtained above was placed at the bottom of a cubic cell with linear dimensions 60, 80 and 100 Å for the clusters comprising 256, 500 and 864 atoms, respectively. Then, a defect-free
graphene sheet with 640, 1144 and 2560 carbon atoms was deposited onto the metal clusters with 256, 500 and 864 atoms, respectively. A schematic image of this process is shown in Fig. 1b. A 1DLJ potential with parameters $\sigma = 3.23\text{ Å}$ and $D_0 = 0.5\text{ eV}$ was used between the substrate and the carbon atoms in the graphene sheet in order to prevent it from becoming wrinkled $[19]$. However, the energy gain caused by this interaction was not counted towards the interaction energy between the graphene sheet and metal cluster. After the graphene sheet covered the metal cluster, the graphene sheet was annealed for 20 ps at 1500 K. During annealing, the atoms of the metal cluster were fixed at 0 K in the same manner as for the calculations using crystallographic metal facets, as described in Section 3.1.

The ideal energy of interaction between graphene sheet and metal cluster was calculated from the difference between the total energy of the metal cluster covered by the graphene sheet and the sum of the energies of isolated (but unrelaxed) metal cluster and graphene sheet. The energy of the isolated graphene sheet was calculated using the final atomic configuration produced by the annealing process when it had been removed from the metal cluster. The interaction energy was then divided by the surface area of the metal cluster, derived from the contact angle, to obtain the interaction energy per unit area. Fig. 6b shows the plots of the interaction energy per unit area ($\text{Å}^2$) against contact angle. It was found that interaction energy per unit area was systematically independent of contact angle, although it does display a large deviation from its average value. The average of the interaction energies for the nickel, cobalt and iron clusters were 0.948, 1.694 and $2.234\text{ eV} \text{ Å}^{-2}$, respectively. In particular, the interaction energy for iron clusters was found to be more than twice that derived for nickel clusters. This trend agrees with the interaction energy between the annealed graphene sheet and the bulk crystalline metal surfaces discussed in Section 3.1. It is important to note that the deviations from the average values shown in Fig. 6b are not simply random fluctuations, but are systematically related to the type of surface faceting displayed by each cluster configuration. Due to the relatively small sizes of clusters, each can display a mixture of close-packed and other types of facet, which in turn lead to different surface interaction energies as shown in Section 3.1. Thus, clusters with large negative deviation from the appropriate mean interaction energy tend to have more close-packed facets, whereas those with large positive deviations tend to be more amorphous or have crystalline facets which are not epitaxial to the graphene sheet.

The reason why the interaction energy calculated is so different between three metals is related to the number of defects present in the graphene sheet when it is absorbed to the cluster. Fig. 7 shows the snapshots of the graphene and metal cluster with 256 atoms after annealing, with the parameter for the 1DLJ, $D_0 = 1.25\text{ eV}$. The contact angles of these clusters sampled were $82.16^\circ$ for nickel, $84.64^\circ$ for cobalt and $84.73^\circ$ for iron, respectively. In the case of the nickel cluster, no defects were observed in the graphene sheet, although a small number of pentagons and heptagons were observed at the fold in the graphene where it meets the substrate. On the other hand, there were many more defects in the graphene sheet adsorbed to the cobalt and iron clusters. In the former case, we found that there were few [0001]$_{\text{hcp}}$ type facets on the surface of the cobalt particle, whereas in the case of iron this was due to the relatively strong interactions with the predominantly [001]$_{\text{bcc}}$ type facets of the cluster. Thus, the high interaction energy of the graphene sheet is due to defects stabilized by interaction with the surface of the metal cluster, which accounts for the large differences in average interaction energy observed between the different metal clusters and the graphene sheet.

4. Conclusions

In summary, the graphitization ability of several transition metals commonly used as catalysts for carbon nanotube growth (nickel, cobalt and iron) has been investigated via classical molecular dynamics simulation. First, the stability of the graphene on the surfaces of the bulk crystalline metals was examined. After some initial bond breakage in the graphene due to kinetic energy of impact with the metal surface, the hexagonal carbon network was rapidly reconstructed on the Ni[111]$_{\text{bcc}}$ and Co[0001]$_{\text{hcp}}$ surfaces, whereas the graphene structure was not readily recovered on the Fe[100]$_{\text{bcc}}$ surface. This is due to the fact that a two-
A dimensional closed-packed facet can act as a template for reconstructing the graphene structure due to the epitaxy. Next, the interaction between graphene and metal clusters was examined. Due to the relatively strong interactions with the predominantly \{100\}_{bcc} type facets of the iron cluster, the surface energy of graphene on iron was calculated to be twice that of the cobalt and nickel clusters. In the case of cobalt clusters, the interaction energy was higher than for nickel due to reduced propensity for forming close-packed facets. The calculated differences in interaction energy of metal clusters with graphene sheet can lead to various consequences for the carbon nanotube growth process. As shown by our recent Monte Carlo (MC) modelling study [20], a strong interaction energy between the graphene sheet and catalytic metal cluster can lead to double-wall CNT growth, whereas only single-wall CNTs were formed in the case of a weak interaction. However, this does not take into account the ability of the metal surface to nucleate the graphene sheet in the first place and, in the present study, we have found that nucleation occurs more easily on surfaces with lower interaction energy that have good epitaxy with the graphene. Therefore, it is likely that the ideal conditions for experimental growth of nanotubes may lie somewhere between these two extremes, and our study emphasizes the importance of a detailed understanding of the structure of catalytic nanoparticles and achieving good control of their surface structure in order to produce tubes with a consistent geometric structure.

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