

# Growth Energetics of Single-Wall Carbon Nanotubes with Carbon Monoxide

Kwanyong Seo, Changwook Kim,<sup>†</sup> and Bongsoo Kim\*

Department of Chemistry, KAIST, Daejeon 305-701, Korea

Young Hee Lee

Center for Nanotubes and Nanostructures Composites, Institute of Basic Science, Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea

Kihyung Song\*

Department of Chemistry, Korea National University of Education, Chongwon, Chungbuk 363-791, Korea

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The microscopic growth energetics of single-wall carbon nanotubes (SWNTs) with gas-phase CO molecules is investigated. Our density functional calculations show that CO molecules can form carbon networks directly at an open edge of SWNT by adsorption and subsequent desorption procedure. CO molecules adsorb to the carbon atom in an open edge of the SWNT, not through the oxygen atom but through the carbon atom, because the frontier orbital of the CO molecule has more carbon character. Such adsorption results in the formation of a carbon–carbon bond. Formation of a hexagonal carbon ring is thermodynamically more favorable than that of a pentagonal carbon ring and becomes a driving force for the growth of SWNTs. A possible growth mechanism through formation of hexagonal ring structure is suggested from the results of this study. Our results of energy calculations suggest that growth in the direction of a zigzag wall is more favorable. The roles of a catalyst, which nucleates the growth of SWNT and stabilizes an open edge with dangling bonds, are further discussed.

## I. Introduction

Very high chemical stability and mechanical strength made the carbon nanotube a very important material in nanotechnology. The most active research area using carbon nanotubes includes applications to nanodevices, field emitters, gas sensors, hydrogen storage in fuel cells, and DNA recognition technology.<sup>1–6</sup>

Though single-wall carbon nanotubes (SWNTs) have different electronic properties depending on their chirality and diameters,<sup>7</sup> it is difficult to selectively synthesize SWNTs that have appropriate electronic properties for each application. A practical method to overcome these difficulties can be, for example, to synthesize SWNTs and then remove undesired types by an etching method,<sup>8</sup> or to modify synthesized SWNTs by hydrogenation and fluorination,<sup>9–11</sup> to provide desired electronic properties. The electronic structure of SWNTs is determined in the growth process but the detailed process is not yet known. Understanding the growth mechanism would be very helpful in getting SWNTs with desired electronic properties. Previous studies about a growth mechanism tried to verify the general role of catalysts in nanotube growth<sup>12,13</sup> and determine the growth process by spectroscopic methods in real time.<sup>14</sup> These macroscopic approaches, however, did not help much to understand the structure formation mechanisms and electronic properties of SWNTs. Therefore, microscopic study of the growth mechanism at a molecular level using theoretical

methods can play an important role in the deployment of SWNTs.

Theoretical microscopic studies on the growth of SWNTs have been performed on the role of catalysts,<sup>15</sup> nucleation,<sup>16</sup> and growth mechanism using a classical molecular dynamics (MD) method.<sup>17</sup> However, the *ab initio* method has not been used much for the study of energetics on the chirality-selective mechanism of SWNTs at a molecular level.

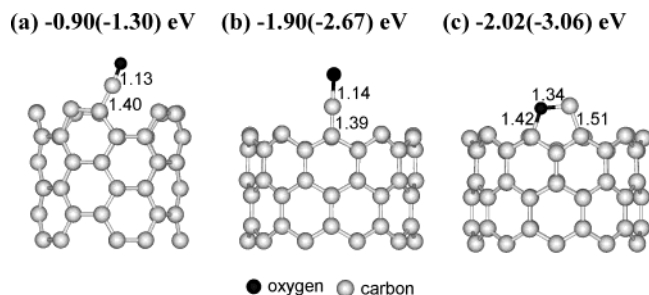
In this study, the growth mechanism of SWNTs by carbon monoxide gas as a carbon supplier is investigated thermodynamically using density functional calculations. Since the first suggestion of a synthesis method,<sup>18</sup> there were parametric studies to determine the conditions that affect the synthesis.<sup>19</sup> Although a detailed growth mechanism has not been fully understood, it is known that carbon is supplied by the Boudouard reaction<sup>20</sup> in the gas phase or at the surface of a catalyst, and this process is affected by the existence and type of catalysts. It was suggested that growth of SWNTs can proceed via adsorption of carbon monoxide at the open edge of a carbon nanotube.<sup>17</sup> In this case, catalyst can assist the reaction by stabilizing the unstable tube edge. The purpose of this study is to investigate the energetics and processes of carbon supply from gas and formation of a carbon network. A total growth mechanism is also proposed.

## II. Computational Details

We considered single-wall zigzag (10,0) and armchair (5,5) nanotubes with an open edge.<sup>27</sup> The diameters of the nanotubes are 7.9 and 6.8 Å, respectively, and the average bond length is 1.42 Å. Ten and eight carbon layers along the tube axis (*z*-

\* Corresponding author. E-mail: (B.K.) bongsoo@kaist.ac.kr, (K.S.) ksong@pchem.knue.ac.kr.

<sup>†</sup> Also with Corporate R&D center, Samsung SDI Co., Ltd. 428-5, Yongin, 449-902, Korea.

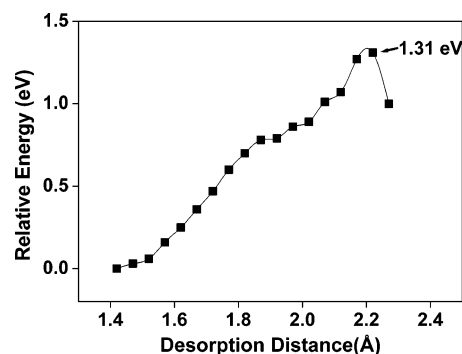


**Figure 1.** Adsorption of a CO molecule on (a) the armchair edge and (b), (c) the zigzag edge. Dark and gray balls indicate the oxygen and carbon atom, respectively. The adsorption energies are shown in the figure. Numbers are results from SCC-DFTB, and the numbers in parentheses are those from GGA.

directions) were used for armchair and zigzag tubes, respectively.<sup>21</sup> Open-ended edges were chosen to see an adsorption effect, and bottom dangling bonds were saturated by hydrogen atoms to minimize the edge effect.<sup>3</sup> We used a self-consistent charge-density-functional-based tight-binding (SCC-DFTB) method<sup>22</sup> to determine the most stable geometries. Various adsorption sites of each molecule on both nanotubes are investigated by computationally less demanding tight-binding calculations. Our total energy calculations and corresponding structure optimizations of the most stable geometries are based on the density functional formalism within the generalized gradient approximation (GGA), as implemented in DMol3 code,<sup>23</sup> and the semiempirical method Austin model 1 (AM1)<sup>24</sup> is also used to compare with density functional results. We define the adsorption energy of molecules as  $E_{\text{ad}} = E_{\text{tot}}(\text{gas} + \text{CNT}) - E_{\text{tot}}(\text{gas}) - E_{\text{tot}}(\text{CNT})$ , where  $E_{\text{tot}}$  is the total energy of a given system. All electron Kohn–Sham wave functions are expanded in a local atomic orbital basis set with each basis function defined numerically on an atomic-centered spherical polar mesh. We used a double numeric polarized basis set, which is the most complete set available in the DMol3 code. In this basis set, the 2s and 2p carbon orbitals are represented by two wave functions each, and 3d (2p) type wave functions on each carbon (hydrogen) atom are used to describe the polarization. No frozen core approximation is used throughout the calculations. The forces on each atom to be converged during each relaxation are less than  $10^{-3}$  au.

### III. Results and Discussions

**A. Adsorption Geometry.** We investigated adsorption of CO molecules at various sites in armchair and zigzag tube edges. For an armchair tube, as shown in Figure 1a, only the carbon atom of CO forms a bond with the carbon atom of an armchair tube edge. This result is different from the previous study in which other gases possessing an oxygen atom make a bond between the oxygen atom and the carbon atom of an armchair tube edge.<sup>8,25,26</sup> This can be explained by the shape of frontier orbital of CO that has more carbon character than oxygen.<sup>27</sup> The calculation using SCC-DFTB gave an adsorption energy of  $-0.90$  eV, whereas the GGA method gave  $-1.30$  eV. For a zigzag tube, a carbon–carbon bond is similarly formed as in an armchair case, and the adsorption energy is  $-1.90$  eV by SCC-DFTB and  $-2.67$  eV by GGA, as shown in Figure 1b. Another structure, which forms a pentagon shape as shown in Figure 1c, is more stable with an adsorption energy of  $-2.02$  (SCC-DFTB) and  $-3.67$  eV (GGA). It is well-known that the edge of a zigzag tube is less stable than that of an armchair tube.<sup>28</sup> For the two different structures of CO adsorbed on a zigzag tube, the structure shown in Figure 1c has a larger

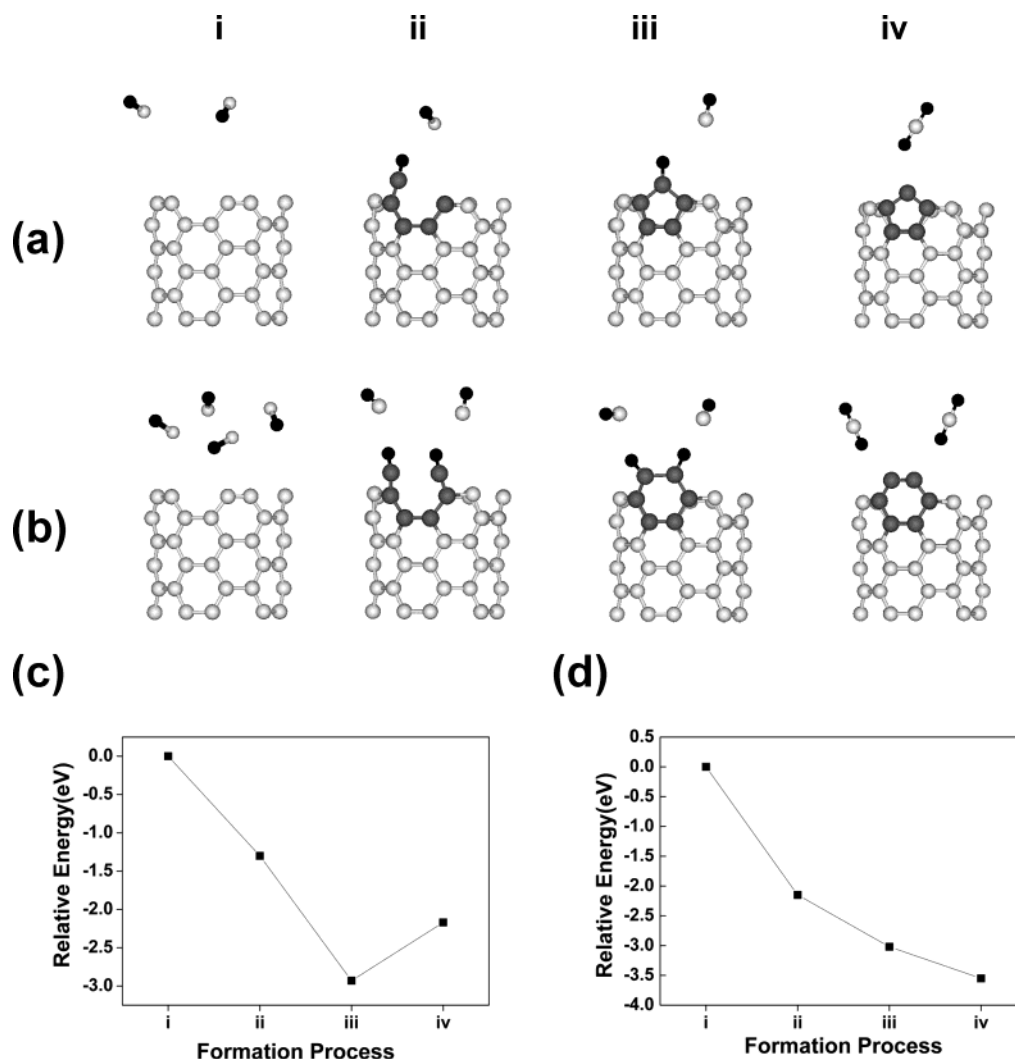


**Figure 2.** Desorption energy barrier of change from the structure of Figure 1c to that of Figure 1b. All other notations are as in Figure 1.

adsorption energy than that in Figure 1b. It is due to the fact that the surface can be stabilized by the formation of two bonds between edge carbons and CO. This is similar to the case where  $\text{CO}_2$  gas is adsorbed to the edge of SWNT.<sup>8</sup> Actual growth would proceed through the structure of Figure 1b, because the structure with two CO molecules adsorbed is much more stable than those of Figure 1b,c, which will be discussed in the following section of this paper. Also, as shown in Figure 2, even though an energy of 1.31 eV is necessary to change the structure of Figure 1c to that of Figure 1b, this change could occur easily at the high pressure and high-temperature condition of an actual synthesis.<sup>18</sup> As a result, structures of Figure 1a,b can be regarded as a first step to form carbon networks for the growth of SWNTs.

**B. Growth Energetics.** Figure 3 shows the growth process and energetics of carbon network formation by adsorption of CO gas at the open edge of an armchair tube. As presented in Figure 3a, two CO molecules participate in pentagonal ring formation at an armchair tube edge. Then one CO forms a bond at an edge to form a new carbon network (steps ii and iii). Another CO molecule reacts with an oxygen atom attached to a carbon network (step iv) and desorbs as  $\text{CO}_2$ . The energetics of this process, depicted in Figure 3c, tells us that this process is spontaneous up to step iii, except for step iv, the desorption of  $\text{CO}_2$ . On the contrary, the process of hexagonal ring formation, shown in Figure 3d, is a stabilizing one throughout the entire process. As shown in Figure 3b, four CO molecules are needed to form a hexagonal ring in the reaction. Two CO molecules adsorb at the edge of an armchair tube (step ii) and form a new carbon network (step iii). Two additional CO molecules react with two oxygen atoms in the network and desorb as  $\text{CO}_2$  (step iv). It is considered that the formation of a pentagonal ring makes the cap that stops the growth, and the hexagonal ring formation keeps the growth process going. We suggest that the growth process by a hexagonal ring formation is a preferred one to the stopping process by a pentagonal ring-formation judged by the energetics presented in Figure 3. This could be one of the driving forces for the SWNT growth.

The process of carbon network formation by CO adsorption to an open edge of a zigzag tube is presented in Figure 4. Pentagonal ring formation requires four CO molecules, as shown in Figure 4a. Two CO molecules first adsorb at a zigzag tube edge (step ii) and form a new carbon network (step iii). Two additional CO molecules take out the top oxygen atoms in the network as  $\text{CO}_2$ , as in an armchair tube case. The energetics, shown in Figure 4c, displays similar behavior to the pentagonal ring formation in an armchair tube case. Hexagonal ring formation at an open edge of a zigzag tube is shown in Figure 4b, and it is similar to other ring formation processes except that the required number of carbon molecules is six. As depicted



**Figure 3.** Suggested growth mechanism on an armchair edge and its energetics with a CO molecule: (a) pentagonal ring formation process; (b) hexagonal ring formation process; (c) energetics of (a); (d) energetics of (b). All other notations are as in Figure 1.

**TABLE 1: Calculated Energies for Armchair Tube from the AM1, DFTB, and GGA Calculations<sup>a</sup>**

	formation steps			
	i	ii	iii	iv
Pentagon Formation Process				
AM1	0	-5.81	-5.05	-3.68
DFTB	0	-0.90	-1.25	+0.27
GGA	0	-1.30	-2.93	-2.17
Hexagon Formation Process				
AM1	0	-8.50	-7.17	-6.52
DFTB	0	-1.33	-0.82	+0.10
GGA	0	-2.15	-3.02	-3.55

<sup>a</sup> All energies are in electronvolts.

**TABLE 2: Calculated Energies for Zigzag Tube from the AM1, DFTB, and GGA Calculations<sup>a</sup>**

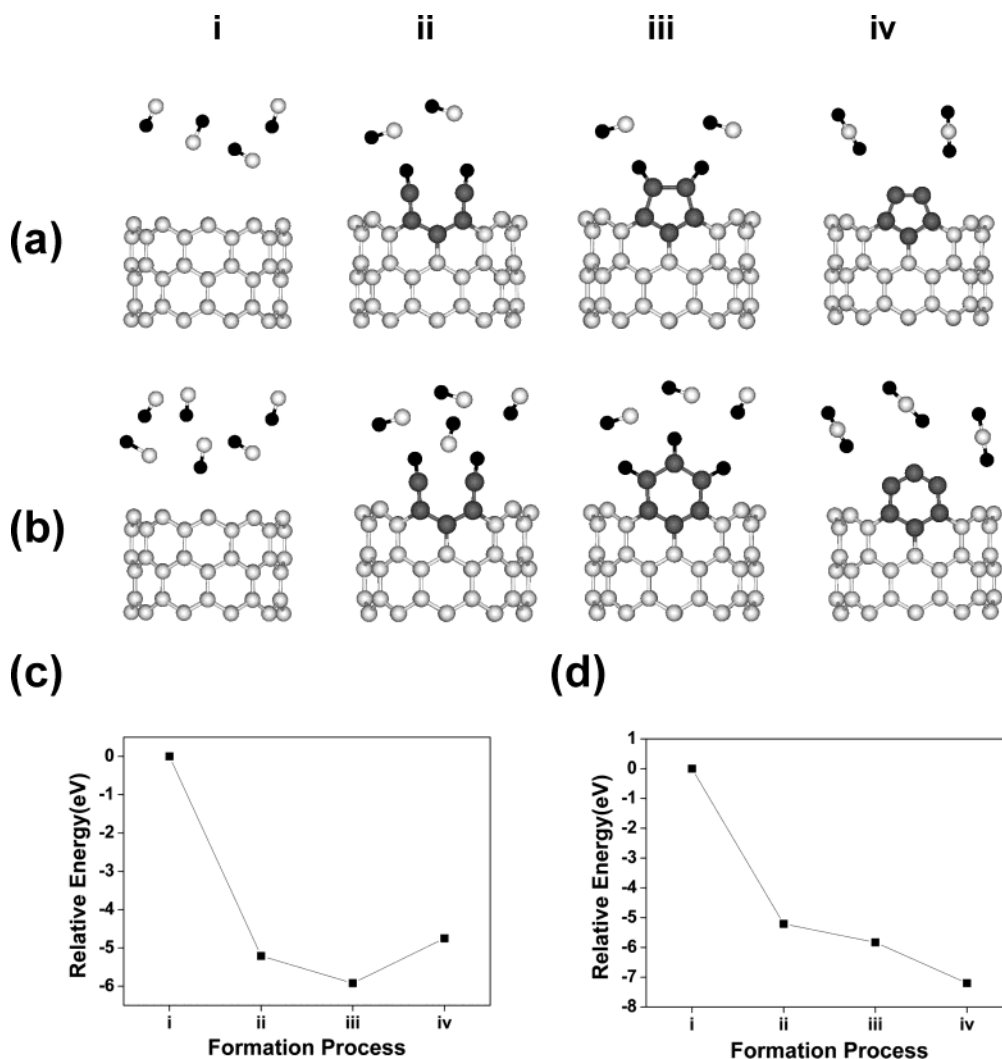
	formation steps			
	i	ii	iii	iv
Pentagon Formation Process				
AM1	0	-6.86	-7.48	-4.13
DFTB	0	-3.15	-3.37	-0.70
GGA	0	-5.21	-5.92	-4.75
Hexagon Formation Process				
AM1	0	-6.83	-6.35	-6.68
DFTB	0	-3.15	-2.73	-1.29
GGA	0	-5.21	-5.83	-7.20

<sup>a</sup> All energies are in electronvolts.

in Figure 4c,d, the pentagonal ring formation that puts a cap to stop the SWNT growth, is less preferred than the hexagonal ring formation process that continues the growth. The energetics of both the armchair and zigzag tubes show a similar trend, but the energy values are quite different. This will be explained in detail when the values given in Tables 1 and 2 are compared.

**C. Adsorption Barrier.** We have shown that the adsorption of a CO molecule occurs first and is an important process for the formation of a new carbon network at an open edge of SWNTs. Figure 5 shows the CO adsorption barrier for various processes. Figure 5a shows that there is no adsorption barrier when a CO molecule adsorbs at an armchair edge. Figure 5b

shows that the zigzag tube also has no adsorption barrier. A previous semiempirical study gave the same results.<sup>17</sup> The adsorption of an oxygen molecule, which is one of the most widely used molecules for purification of carbon nanotubes,<sup>29</sup> gave similar results.<sup>30</sup> In addition, there is no barrier for simultaneous adsorption of two CO molecules at a SWNT, as shown in Figure 5c,d. It is also known that there is no adsorption barrier when CO molecules adsorb successively at an edge of armchair and zigzag tubes.<sup>27</sup> This tells us that the CO adsorption at an open edge of SWNTs does not require any energy and hence occur spontaneously. This is also true when two or more CO molecules adsorb. Therefore, we concluded that CO



**Figure 4.** Suggested growth mechanism on a zigzag edge and its energetics with a CO molecule: (a) pentagonal ring formation process; (b) hexagonal ring formation process; (c) energetics of (a); (d) energetics of (b). All other notations are as in Figure 1.

molecules can easily adsorb at an open edge of tubes in the SWNT growth process, forming new carbon networks, as shown in Figures 3 and 4.

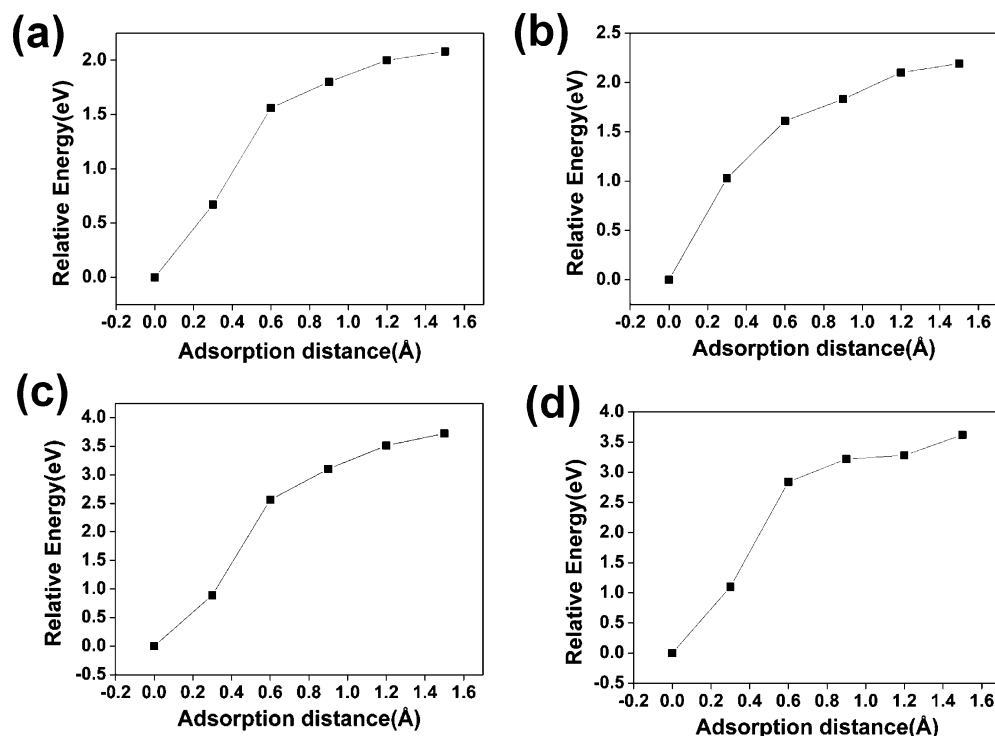
**D. Calculated Energy.** The values of adsorption energies for steps i–iv of Figure 3, relative to step i, are given in Table 1. The results are calculated using DFTB, GGA, and semiempirical AM1 methods. The DFTB method gave similar results to those from GGA, a more accurate method. Various calculation methods give different values of the change of energy. DFTB calculation shows that step iv energy is higher than even the initial state i in hexagonal ring formation, whereas the GGA calculated adsorption energies are steadily more stabilized throughout the whole process. The semiempirical AM1 gave quite different values, whereas the observed trend is similar to those in DFTB case. These AM1 energies are much larger in absolute values than the GGA results and the relative trend is different from the GGA results as well. Considering the fact that GGA usually gives more accurate results than DFTB or AM1 methods, it is necessary to perform density functional calculations to reproduce realistic values.

Table 2 shows the energy values for the steps in Figure 5. The same trends can also be seen in Table 2. Note that the adsorption energy of CO gas on a zigzag tube is larger than that on an armchair tube. For example, for the energy of step ii of hexagonal ring formation a zigzag tube gave  $-3.15$  eV (DFTB) and  $-5.21$  eV (GGA), which are more than twice the

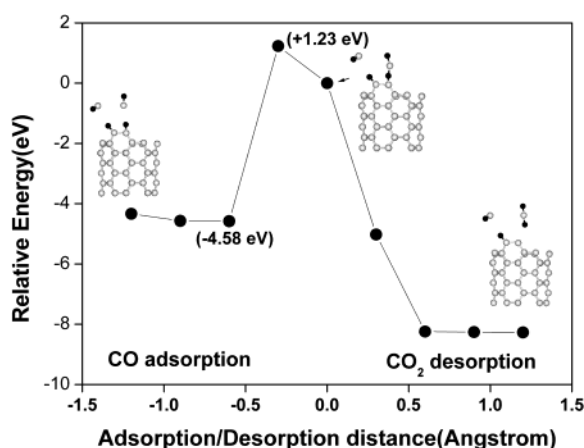
values in an armchair case (DFTB,  $-1.33$  eV; GGA,  $-2.15$  eV). This tells us that, in the synthesis of SWNTs using CO gas, a zigzag tube could be a preferred product to an armchair tube. It is reported that the chiral angles of synthesized tubes (excluding armchair and zigzag tubes) are in the range  $3\text{--}12^\circ$ ,<sup>31</sup> which are close to those of zigzag tubes. It has also been suggested that zigzag tubes would grow faster than armchair tubes if the SWNTs were nucleated on catalyst particles.<sup>18</sup> Hence, this result suggests a possibility of synthesis of SWNTs using CO gas, which could select the chirality.

The results presented above show that a new carbon network can be formed by adsorption of CO gas at an open edge of SWNTs. It should be noted that there is no barrier for this adsorption process. The growth process of a carbon network is energetically more favorable than the stopping process. Figure 6 shows the activation energy necessary to take out the top oxygen atoms in a newly formed carbon network as  $\text{CO}_2$ . We considered the hexagonal ring structure that was formed at the edge of an armchair tube. This graph represents the process in which one of two top oxygen atoms is desorbed as  $\text{CO}_2$  after reaction with a CO molecule. As already described, the energy of the total process was steadily decreased as in Figure 3. When CO forms a bond with a top oxygen atom, however, it is close to a transition state and very unstable. The activation energy is about  $5.8$  eV, which is hard to overcome at the experimental temperature.<sup>18</sup> Hence, it is necessary to consider the role of a





**Figure 5.** Adsorption energy barrier when a CO molecule adsorbs on (a) the armchair edge and (c) the zigzag edge and when two CO molecules simultaneously adsorb on (b) the armchair edge and (d) the zigzag edge.



**Figure 6.** Activation energy for the desorption of the top oxygen atoms as  $\text{CO}_2$  after forming a hexagonal ring structure on an armchair edge. All other notations are as in Figure 1.

catalyst in this process. In experiments, the synthesis of SWNTs requires a catalyst. From the high activation energy presented in Figure 6, we suggest that a catalyst could stabilize the energy of the SWNT edge, which becomes very unstable in the process of synthesis.<sup>32</sup> Previous theoretical study<sup>17</sup> of the growth of SWNTs suggested that CO molecules are more stable when they adsorb on an open edge of SWNT than on a metal cluster such as  $\text{Fe}_{18}$  used as a catalyst, thus providing carbon atoms necessary for the growth of a carbon network. As a result, a catalyst, participating in the nucleation process at the beginning of SWNT growth, would not facilitate atomization of CO to produce carbon atoms necessary for the growth. Rather, it would play an auxiliary role to stabilize the energy of a tube edge. Although the catalyst is known to be very essential for the growth of SWNTs, the effect of metal catalysts was not studied in this research due to some practical difficulties in the calculations. The conclusion of this study about the role of catalyst may be

related with one of the possible processes for the synthesis of SWNT with catalysts. For more conclusive discussion, the calculations which include metal catalyst are necessary.

#### IV. Summary

We investigated the adsorption of CO molecules on SWNT edges and followed the growth mechanism of SWNT using density functional calculations. We propose a reasonable growth mechanism and its energetics of a (5,5) armchair tube and a (10,0) zigzag tube.

The carbon atom in CO forms a bond with the carbon of nucleated SWNT tube edge when the CO molecule adsorbs on an edge of a nanotube. This adsorption structure can be considered as a first step to form carbon networks for the growth of SWNTs.

The process of hexagonal ring formation is thermodynamically more favorable than that of pentagonal ring formation. We suggest that the formation of a pentagonal ring makes a cap that stops the growth, and a hexagonal ring formation keeps the growth process going. This could be one of the driving forces for the SWNT growth.

According to the energy calculation results, the growth in the direction of a (10,0) zigzag tube wall is more favorable than that of a (5,5) armchair tube. This result suggests the possibility of chirality-selective growth of SWNTs using CO gas.

The role of a catalyst would be reduction of the activation energy by stabilization of tube energy and not to supply carbon atoms by atomization of CO. For a definite conclusion, more research needs to be done on the role of metal catalyst.

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**Supporting Information Available:** Figure S1 (model of the (5,5) armchair (left) and (10,0) zigzag (right) nanotubes terminated with hydrogen atoms at one end), Figure S2 (local charge densities of (a) HOMO and (b) LUMO: the CO gas molecule), and Figure S3 (adsorption energy barrier when two CO molecules adsorb successively on (a) the armchair edge and (b) the zigzag edge). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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