

Influence of partial pressure on base-growth of single carbon nanotube



M. Saeidi*

Department of Physics, Faculty of Basic Science, Shahed University, Tehran, Iran

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ABSTRACT

Influence of hydrocarbon partial pressure on single carbon nanotube (CNT) growth in chemical vapor deposition is investigated by a new theoretical model based on kinetic theory of gases and, phonon vibrations of carbon nanotube on catalyst. Results show that CNTs with larger diameter grow lesser owing to higher damping factors and CNT inertia. In addition, an optimum temperature for the growth is obtained for a CNT with a specific diameter and catalyst. Also it is shown that the optimum temperature is changed by using different catalysts. Finally effect of the partial pressure on the growth is also discussed. It is demonstrated that increasing partial pressure leads to the longest CNTs and also, influence of partial pressure on CNTs with smaller diameters is stronger. All results of the presented mechanism are in good agreement with reported experimental results.

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1. Introduction

According to relation between carbon nanotube (CNT) structure and their physical, chemical and mechanical properties [1–3], control and optimization of production methods of these structures and detection of effective parameters in their growth are the most important research subjects in CNT science [4–16]. To approach this aim, their growth mechanism in various production methods must be understood. In recent years, the most practical production method has been the chemical vapor deposition (CVD) [17–23]. Up to now, several research studies have been done to describe some concepts of growth mechanism i.e. preparation mechanism of catalyst and substrate to start growing [22,24–27], conditions for base-growth and tip-growth [21,28], etc. Recently, we presented a theory to describe growth mechanism of single CNT in CVD [4]. The theory is based on phonon vibrations of single CNT on catalyst in base-growth and includes some parameters such as catalyst type, temperature, CNT diameter, etc. Considering influence of another important parameter means partial pressure of decomposed hydrocarbons, in addition to some corrections in our previous model, cause a new model which is presented in this paper.

2. Model and theory

Because of the van der Waals bond with catalyst, a CNT oscillates longitudinally on catalyst during its growth. When the distance

between CNT and catalyst is more than the diameter of carbon atom, a carbon may involve between the catalyst and tube for a further growth of the tube. It is thus expected the critical amplitude of CNT oscillation, A_{osc} , must be equal to the diameter of carbon atom for a further growth from the current stage. Van der Waals interaction between CNT and its catalyst is simulated by a spring, meanwhile a CNT is simulated by a mass $M(t)$ which is increasing during the growth in the theory. Fig. 1 illustrates the phonon vibration of a CNT and its interaction with the catalyst by a spring–mass system.

The growth of a CNT is described by loops and each loop is made of numbers of carbon atoms N . Therefore, the mass of the CNT and the numbers of carbon atoms in one loop are written as

$$M(t) = n(t)Nm_C \text{ and } N = \frac{\pi D}{d_{C-C}} \quad (1)$$

where $n(t)$, m_C , D and d_{C-C} are the number of loops that is increasing during the growth, the mass of a carbon atom, the CNT diameter and carbon–carbon bond length in each loop, respectively. Because only the first loop interacts with catalyst, the spring coefficient representing the van der Waals interaction between each wall and substrate, K , is provided to be

$$K = Nk \quad (2)$$

where $k = 2E_{osc}/A_{osc}^2$, and E_{osc} and k are energy of oscillation and spring coefficient between a carbon atom and the catalyst, respectively. It is obvious that the number of loops, $n(t)$, is a function of the angular frequency of the oscillation, $\omega(t)$, and time, which is shown in the following expression:

$$n(t) = \frac{\omega(t)}{2\pi N} t \quad (3)$$

* Tel.: +982151212271.

E-mail addresses: Saeidi.mr@gmail.com, M.Saeidi@shahed.ac.ir

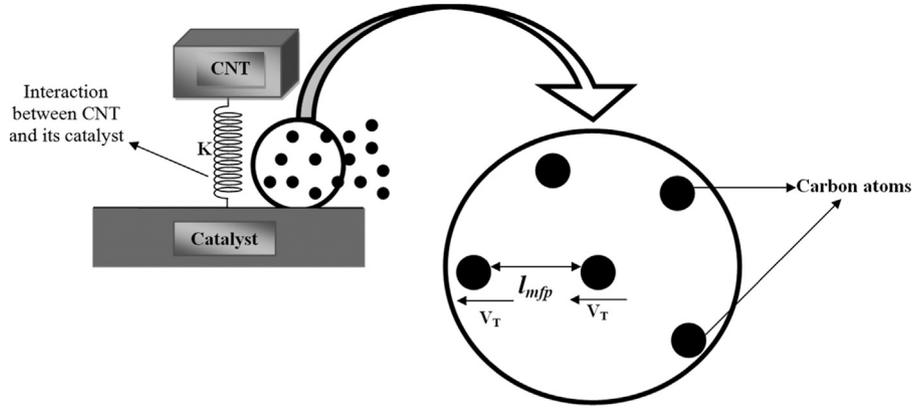


Fig. 1. Model of CNT and its catalyst by a mass–spring system. Decomposed carbon atoms have a thermal velocity V_T under partial pressure, P , and environmental temperature, T .

where $\omega(t) = \sqrt{2E_{osc}/n(t)A_{osc}^2m_C}$. From Eq. (3), $n(t)$ can be calculated, and the growth of the CNT is provided to be

$$L(t) = n(t)l_C \quad (4)$$

where $L(t)$ and l_C are CNT length and distance between two loops, respectively. Eq. (4) is obtained without considering the damping effect. To consider the effect of damping due to the environment and any other loss in the system, Eq. (4) should be multiplied by $e^{-\eta t}$ that demonstrates the effect of damping on growth process. The parameter η is the damping factor. The postulation employed in the theory is that the thermal velocity of the immigrant carbon atoms produced by hydrocarbon decomposition, V_T , is not infinity. From the kinetic theory, if immigrant particles have three degrees of freedom, we can have the following equation:

$$\frac{3}{2}k_B T = \frac{1}{2}m_C V_T^2 \quad (5)$$

A coefficient β , representing the probability of binding an immigrant carbon atom to CNT, is considered in the theory as follows:

$$\beta = \frac{t_{c(min)}}{t_c} \quad (6)$$

where t_c is time interval between two immigrant carbon atoms and can be calculated by

$$t_c = \frac{l_{mfp}}{V_T} \quad (7)$$

where $l_{mfp} = 1/\sqrt{2}\pi d^2 n_v$ is the mean free path between the two immigrant carbon atoms and d is the diameter of carbon atom which is equal to the amplitude of oscillation, A_{osc} . Because the partial pressure is low, the gas of immigrant carbon atoms can be considered as an ideal gas in which the n_v is equal to $P/(k_B T)$. The parameter P is partial pressure of decomposed hydrocarbons. The constant parameter $t_{c(min)}$ in Eq. (6), is minimum meaningful time interval between the two immigrant carbon atoms which is considered equal to 10^{-12} s. Also the relation of E_{osc} with temperature, T and van der Waals bond energy between CNT and catalyst, U_{IJ} is provided to be

$$E_{osc} = E_0 \exp\left(\frac{\gamma U_{IJ}}{(1/2)k_B T}\right) \quad (8)$$

where U_{IJ} and γ are Lennard-Jones potential and heat capacity ratio, respectively. If E_0 , in comparison with U_{IJ} , is large, CNT cannot oscillate and will be detached from the catalyst. Therefore, $E_0 = 0.01|U_{IJ}|$ is proposed in the model. The expression for growth is finally obtained from Eqs. (1)–(8) as follows:

$$L = \left(\frac{0.03A_{osc}d_{C-C}t_{c(min)}\sqrt{|U_{IJ}|}e^{\gamma U_{IJ}/k_B T}}{\pi D m_C}\right)^{2/3} \left(\frac{P}{k_B T}\right)^{1/3} t^{2/3} e^{-\eta t} l_C \quad (9)$$

3. Numerical results

3.1. Growth of CNT with different diameters

The variation of the length of the CNT with different diameters versus time, based on Eq. (9), is plotted in Fig. 2 with the following parameters: $A_{osc} = 0.77 \text{ \AA}$, $l_C = 1.5 \text{ \AA}$, $d_{C-C} = 1.42 \text{ \AA}$, $k_B = 1.381 \times 10^{-23} \text{ J/K}$, $t_{c(min)} = 10^{-12} \text{ s}$, $m_C = 19.926 \times 10^{-27} \text{ kg}$, $\eta = 1.5 \times 10^{-4} \text{ s}^{-1}$, U_{IJ} (between carbon and iron) = -2.402 kJ/mol , γ (for ideal gas) = $5/3$, $P = 0.76 \text{ Torr}$ and $T = 700 \text{ }^\circ\text{C}$.

According to Fig. 2, no growth is observed during the first minutes of synthesis and the growth of CNTs is saturated at a certain moment, which was also demonstrated experimentally by Cui et al. [29] and Lee et al. [30]. Single CNT growth is saturated because of two reasons. First, mass of CNT is increased over time. So, the frequency of CNT oscillation on catalyst is reduced and consequently, the growth is saturated over time. Second reason is damping factors such as friction. In addition, it is found that CNTs with larger diameter are saturated more rapidly. The observations are discussed and interpreted as follows. First, because a CNT with larger diameter has more effective surface area, it is more affected by damping factors than CNTs with smaller diameter. Second, a CNT with larger diameter has higher inertia and consequently leads to lower frequency of CNT vibration.

3.2. Optimum temperature for CNT growth

Next, Fig. 3 is provided to describe the variation of the growth of CNT with different diameters versus the temperature with the parameters $A_{osc} = 0.77 \text{ \AA}$, $l_C = 1.5 \text{ \AA}$, $d_{C-C} = 1.42 \text{ \AA}$, $k_B = 1.381 \times 10^{-23} \text{ J/K}$, $t_{c(min)} = 10^{-12} \text{ s}$, $m_C = 19.926 \times 10^{-27} \text{ kg}$, $\eta = 1.5 \times 10^{-4} \text{ s}^{-1}$, U_{IJ} (between carbon and iron) = -2.402 kJ/mol , $\gamma = 5/3$, $P = 0.76 \text{ Torr}$ and $t = 80 \text{ min}$.

Fig. 3 indicates that there is a temperature which optimizes the growth of CNT. For example, for the growth of a carbon nanotube on iron, the optimum temperature is about 973 K. Similar observations were also verified by experimental works [29,31–36]. From Eqs. (5)–(8), when temperature goes up, the oscillation energy of CNT increases. Such an increase of oscillation energy is faster than the increase of t_c and hence the growth is fastened accordingly. However, after a specific temperature, the energy increase will be slower than the increase of t_c and consequently β will decrease leading to slower growth. The optimum temperature can be calculated for obtaining the maximum length of CNTs.

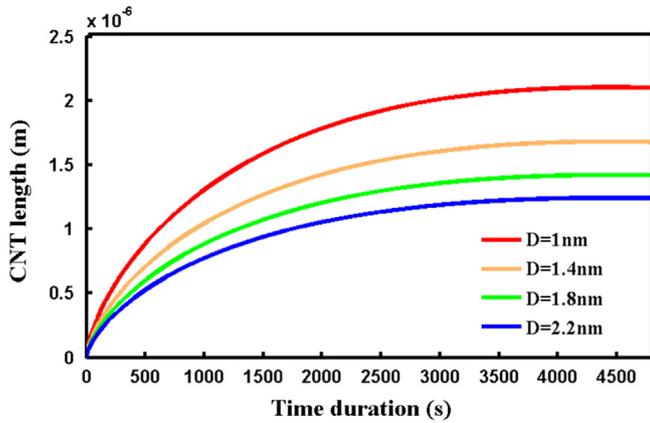


Fig. 2. Growth of CNTs with different diameters at $P=0.76$ Torr and $T=973$ K.

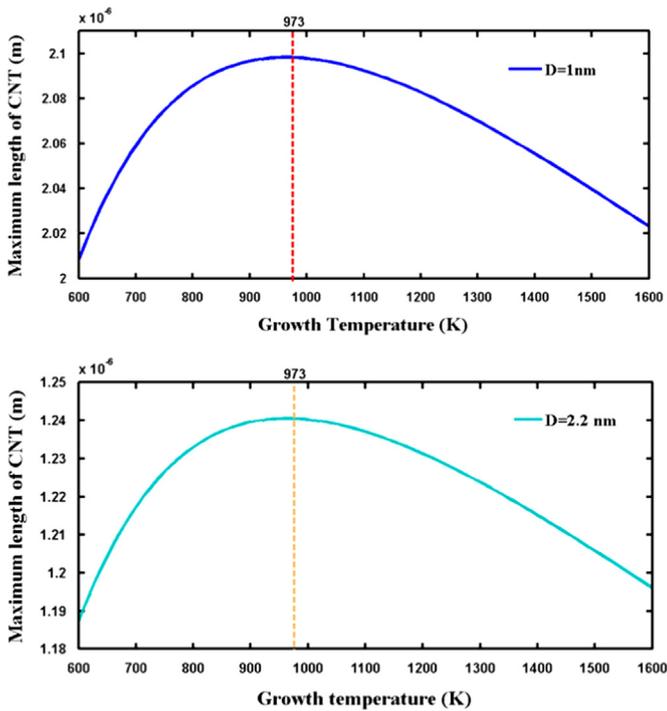


Fig. 3. Dependence of temperature on growth of CNT with different diameters.

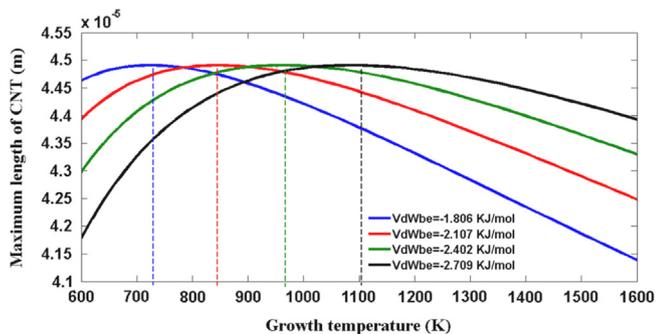


Fig. 4. Dependence of temperature on growth of CNT at different Van der Waals bond energies (VdWbe).

3.3. Dependence of catalysts on CNT growth

Van der Waals bond energy in the model is dependent on the type of catalyst. According to the developed model, the oscillation energy increases with the increase of the van der Waals energy till

a certain value. After this value, the oscillation energy decreases because, at this situation, the bond energy between the carbon and its catalyst is higher than thermal energy which is received by the CNT. Therefore, the CNT motion is limited and, consequently, the growth process is hampered. The variation of the CNT length versus temperature for some van der Waals bond energies (VdWbe) is plotted in Fig. 4 with the parameters $A_{osc}=0.77$ Å, $l_C=1.5$ Å, $d_{C-C}=1.42$ Å, $k_B=1.381 \times 10^{-23}$ J/K, $t_{c(min)}=10^{-12}$ s, $m_C=19.926 \times 10^{-27}$ kg, $\eta=1.5 \times 10^{-4}$ s $^{-1}$, $\gamma=5/3$, $P=0.76$ Torr and $t=80$ min. Fig. 4 shows that there is an optimum catalyst for the growth of CNTs. Existence of an optimum catalyst to optimize CNT growth has also been reported in some papers [36–38].

As it is observed in Fig. 4, there is only one optimum temperature for each type of catalyst. Also it shows the higher the energy, the higher the optimum temperature. For example, the $U_{ij}=-2.402$ kJ/mol is for Fe and related optimum temperature is 973 K [29]. For catalysts with stronger (weaker) U_{ij} , the optimum temperature is higher (lower). Since the increase of the bond energy leads to the motion constraint on CNTs, the optimum temperature for CNT growth increases accordingly. Therefore, when a certain type of catalyst is given, it is possible to calculate the optimum temperature for the CNT growth.

3.4. Dependence of partial pressure on CNT growth

Fig. 5 shows the variation of CNT length versus growth time and partial pressure of decomposed hydrocarbons, based on Eq. (9) with the parameters $A_{osc}=0.77$ Å, $l_C=1.5$ Å, $d_{C-C}=1.42$ Å, $k_B=1.381 \times 10^{-23}$ J/K, $t_{c(min)}=10^{-12}$ s, $m_C=19.926 \times 10^{-27}$ kg, $\eta=1.5 \times 10^{-4}$ s $^{-1}$, U_{ij} (between carbon and iron) = -2.402 kJ/mol, $\gamma=5/3$ and $T=700$ °C.

As it is shown in the Fig. 5, increasing partial pressure leads to increasing CNT length. Increasing partial pressure leads to reducing l_{mfp} and consequently, t_c decreases. Therefore probability of binding increases and CNT grows more. Similar observations are also reported by some papers [39–41].

To investigate relation between diameter of CNT and partial pressure, Fig. 6 is plotted which shows the variation of CNT maximum length versus partial pressure for different diameters with recent parameters and $t=80$ min.

Although the probability of binding increases by increasing partial pressure, but, for CNT with a larger diameter, more carbon atoms must be bond to complete a loop in CNT. Therefore, As Fig. 6 illustrates, for CNT with smaller diameter, influence of partial pressure on CNT length is more.

4. Conclusion

A new theory for base-growth of single CNT in CVD is reported. Results show that the CNT length during growth is saturated due to damping factors and CNT inertia. It is demonstrated there is an optimum temperature for the growth of the CNT and this temperature can be derived from the theory. Also at the optimum temperature, the growth of CNTs with larger diameters is saturated more rapidly because of higher CNT inertia. In addition, relationship between the CNT length and the type of catalyst demonstrates the existence of an optimum catalyst for optimizing the growth of CNTs at a specific temperature. Finally it is shown that increasing partial pressure leads to the longest CNT due to increasing probability of binding. Also it is demonstrated that the influence of partial pressure on CNTs with smaller diameter is stronger. Because all results of the presented mechanism are in good agreement with reported experimental results, so it can be

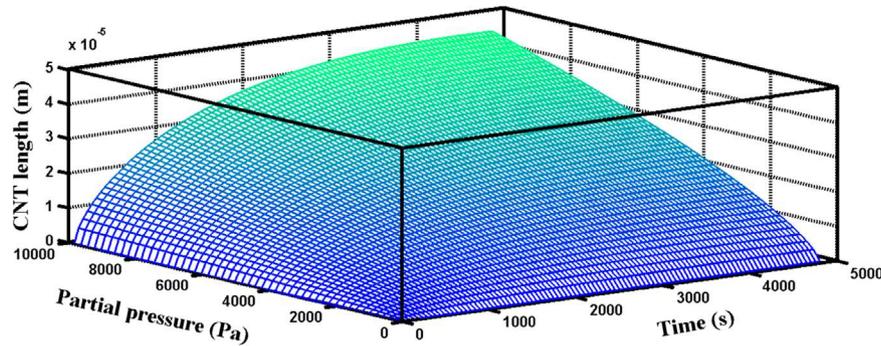


Fig. 5. Dependence of partial pressure on CNT growth.

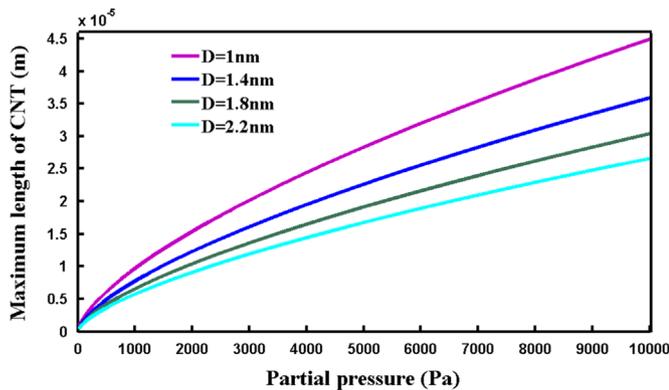


Fig. 6. Relation between CNT diameter and influence of partial pressure on CNT growth.

useful in future experimental and theoretical research studies for optimization of CNT growth.

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