

Tip-growth model of single carbon nanotubes

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Abstract

In this paper, a new model based on kinetic theory of gases and longitude oscillations of metallic nanocluster on single carbon nanotube (CNT) in addition to phonon vibrations of CNT on substrate is presented to describe the growth mechanism of ultra-long CNT in chemical vapor deposition (CVD). Interaction between CNT and catalyst is investigated by Lennard-Jones potential. Simulations demonstrate that metal nanocluster makes and keeps the carbon atoms at tip end reactive. So carbon nanotube can grow more than 1 cm. In addition, results show carbon nanotubes with larger diameter grow less owing to higher damping factors. Furthermore, effect of temperature and type of catalyst on growth is discussed and it is shown that there is an optimum temperature and an optimum catalyst for growth process. Also, it is shown that the optimum temperature is changed by using different catalysts. Finally, effect of the partial pressure of decomposed hydrocarbons on the growth is also discussed. It is demonstrated that increasing partial pressure leads to the longest CNTs and influence of partial pressure on CNTs with smaller diameter is stronger. All results from the model are in good agreement with reported experimental results.

Keywords: Ultra-long carbon nanotubes; Lennard-Jones potential; kinetic theory of gases; phonon vibrations; tip-growth regime; chemical vapor deposition

1. Introduction

Since the discovery of carbon nanotubes (CNTs) (Iijima, 1991), creating long and continuous nanotubes for applications where their properties coupled with extended lengths has been considered (Baughman et al., 2002; Jiang et al., 2002; Zhu et al., 2002; Zheng et al., 2004). In order to fully optimize the production of CNTs, the growth mechanisms involved in their formation must be completely understood. In recent years, the most practical production method has been chemical vapor deposition (CVD) (Kong et al., 1998; Fan et al., 1999; Zhang et al., 2001; Terrones et al., 1997; Rodriguez, 1993; Dai et al., 1996; Jose-yacaman et al., 1993; Gavillet et al., 2001). Up to now, several researches have been done to describe some concepts of growth mechanism i.e. preparation mechanism of catalyst and substrate to start growing (Jose-yacaman et al., 1993; Sinnott et al., 1999; Baker et al. 1972; Baker et al., 1973; Baker et al., 1989), conditions for base-growth and tip-growth (Dai et al., 1996; Cui et al., 2003), etc. A mechanism to describe formation of CNTs in the presence of a metal catalyst has been proposed (Sinnott et al., 1999), which was based on the processes involved in carbon nanofiber formation (Baker et al., 1972; 1978; 1989). For ultra-long CNT, base-growth regime is not responsible and the

tip-growth regime is considered (Zheng et al., 2004; Huang et al., 2004; Moshkalyova et al., 2004; Deck and Vecchio, 2005). It has been proven that in growth of long SWNTs by the fast-heating chemical vapor deposition (CVD), both growth mechanisms coexist, however, only the tip-growth mechanism produces long and oriented nanotubes (Huang et al., 2004). In view of the experimental and simulation works, a comprehensive study to describe the growth mechanism for ultra-long CNTs and the effect of parameter variables, such as the temperature and pressure, on the CNT growth is indispensable. Recently, we presented a theory to describe tip-growth mechanism of single CNT in CVD (Saeidi and Vaezzadeh, 2009). The theory is based on oscillation of a cluster of Fe nanoparticles on CNT and phonon vibrations of CNT on substrate. The theory includes some parameters such as catalyst type, temperature, CNT diameter, etc. Taking the considering influence of another important parameter, partial pressure of decomposed hydrocarbons, into consideration in addition to some fundamental corrections in our previous model, lead to a new model which is presented in this paper.

2. Modeling and mechanism of tip-growth

Owing to the van der Waals bond with catalyst and substrate, a CNT oscillates longitudinally on substrate during its growth and catalyst nanocluster oscillates on CNT tip end. When the distance between CNT and catalyst or CNT and substrate 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 phonon vibrations of CNT and oscillations of metallic nanocluster (MNC), A_{osc} , are equal to the diameter of carbon atom for a further growth from the current stage. Considering Fig. 1, in this model, Van der Waals interaction is simulated by a spring, meanwhile CNT is simulated by a mass $M_{CNT}(t)$ which increase during the growth, and cluster of nanoparticles at tip end of CNT is simulated by a mass M_{MNC} which is a product of the number of nanoparticles in MNC, N_p , and mass of one metallic nanoparticle, m_p , in the theory. Only for simplicity, it is assumed that the interaction between CNT and substrate is the same as the interaction between CNT and MNC. As it will be shown, this assumption is not important in the theory because the dominant and main interaction for ultra-long CNT growth is the interaction between CNT and MNC.

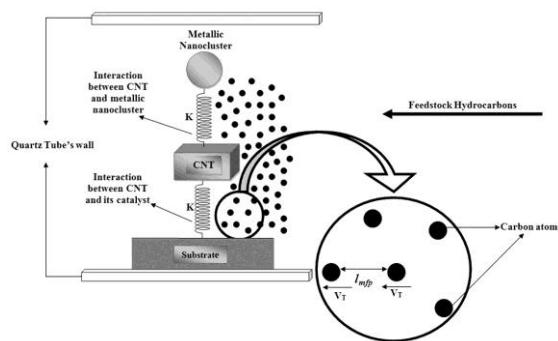


Fig. 1. Simulation of CNT with a MNC at tip end and its substrate by a mass-spring system

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,

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

where $n(t)$, m_c , D and d_{C-C} are the number of loops that increase 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 MNC and substrate, the spring coefficient representing the

van der Waals interaction between CNT and MNC or CNT and substrate, K , is given as

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

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

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

where

$$\begin{cases} \omega = \sqrt{\frac{2NE_{osc}}{A_{osc}^2 N_p m_p}} & ; \text{ for MNC oscillation} \\ \omega = \omega(t) = \sqrt{\frac{2E_{osc}}{A_{osc}^2 n(t) m_C}} & ; \text{ for CNT oscillation} \end{cases}$$

From Eq. (3), $n(t)$ can be calculated for both base- and tip-growth, and the growth of the CNT is given as,

$$L(t) = n_{tot}(t)l_C \quad (4)$$

where $L(t)$, l_C and $n_{tot}(t)$ are CNT length, distance between two loops and total number of produced loops during growth, 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 $e^{-\eta t}$ which demonstrates the effect of damping on growth process. The parameter η is 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 infinite. From kinetic theory, if immigrant particles have three degrees of freedom, the following equation can be obtained:

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

A coefficient β , representing the probability of binding an immigrant carbon atom to CNT, must be multiplied with $n(t)$ for both base- and tip-growth, and 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 $l_{mfp} = \frac{1}{\sqrt{2\pi d^2 n_v}}$ is mean free path between the two immigrant carbon atoms. d is 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 $\frac{P}{k_B T}$. 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_{LJ} is given as,

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

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

$$L(D, T, P, U_{LJ}, t) = \left\{ \left(\frac{0.03 A_{osc} d_{C-C} t_{c(min)} \sqrt{|U_{LJ}|} e^{\frac{\gamma U_{LJ}}{k_B T}}}{\pi D m_c} \right)^{\frac{2}{3}} \left(\frac{P^2}{k_B T} \right)^{\frac{1}{3}} t^{\frac{2}{3}} \right. \\ \left. + \left(\frac{0.03 t_{c(min)}^2 d_{C-C} A_{osc}^2 |U_{LJ}| e^{\frac{2\gamma U_{LJ}}{k_B T}}}{\pi D N_p m_p m_c} \right)^{\frac{1}{2}} \left(\frac{P^2}{k_B T} \right)^{\frac{1}{2}} t \right\} e^{-\eta t} l_c \quad (9)$$

As it is observe in Eq. (9), the first term describes the base-growth of single CNT in CVD by which CNTs grow about 2 mm (Saeidi, 2014). But, according to the Fig. 2, in the presence of the second term which is related to the tip-growth, the CNTs can grow more than 4 cm. This means that the tip-growth is the main and dominant mechanism in growth of ultra-long CNT which has been also shown experimentally (Huang et al., 2004).

3. Numerical results

3.1. Growth of ultra-long CNT with different diameters

The variation of the length of the CNT versus growth time and diameter of CNT, based on Eq. (9), is plotted for iron as MNC and substrate in Fig. 2 with the following parameters: $A_{osc} = 0.77 \text{ \AA}$, $l_c = 1.5 \text{ \AA}$, $d_{C-C} = 1.44 \text{ \AA}$, $k_B = 1.381 \times 10^{-23} \text{ J/K}$, $t_{c(min)} = 10^{-12} \text{ s}$, $m_c = 19.926 \times 10^{-27} \text{ Kg}$, $m_p = 92.769 \times 10^{-27} \text{ Kg}$, $N_p = 40$, $\eta = 1.5 \times 10^{-4} \text{ s}^{-1}$, U_{LJ} (between carbon and iron) = -2.402 KJ/mol , γ (for ideal mono atomic gas) = $\frac{5}{3}$, $P = 0.5 \text{ atm}$ and $T = 973 \text{ K}$.

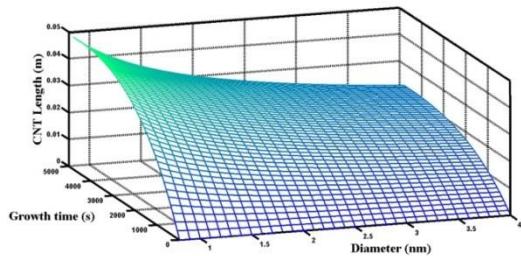


Fig. 2. Growth of CNTs with different diameters at $P=0.5$ atm and $T=973 \text{ K}$

According to Fig. 2, in this situation, a CNT can grow more than 4cm which was also demonstrated experimentally (Zheng et al., 2004). In addition, it is found that the growth of CNTs with larger diameter is saturated more rapidly. The observations are discussed and interpreted as follows. First, Fe-cluster makes and keeps the carbon atoms at tip end reactive. Owing to oscillation of Fe-cluster on CNT, immigrant carbon atoms can be placed between CNT and cluster. So CNT can grow without any limitation. The only limitations in CVD are the size of substrate and damping factors such as friction which leads to growth saturation. Second, because a CNT with larger diameter has great effective surface area, it is more affected by damping factors than CNTs with smaller diameter.

3.2. Optimum Temperature and catalyst for growth of ultra-long CNT

Next, Fig. 3 is provided to describe the variation of the growth of CNT versus the temperature and Lennard-Jones potential with the parameters $A_{osc} = 0.77 \text{ \AA}$, $l_c = 1.5 \text{ \AA}$, $d_{C-C} = 1.44 \text{ \AA}$, $k_B = 1.381 \times 10^{-23} \text{ J/K}$, $t_{c(min)} = 10^{-12} \text{ s}$, $m_c = 19.926 \times 10^{-27} \text{ Kg}$, $m_p = 92.769 \times 10^{-27} \text{ Kg}$, $N_p = 40$, $\eta = 2.2 \times 10^{-4} \text{ s}^{-1}$, γ (for ideal mono atomic gas) = $\frac{5}{3}$, $P = 0.5 \text{ atm}$, $D = 1 \text{ nm}$ and $t = 80 \text{ min}$.

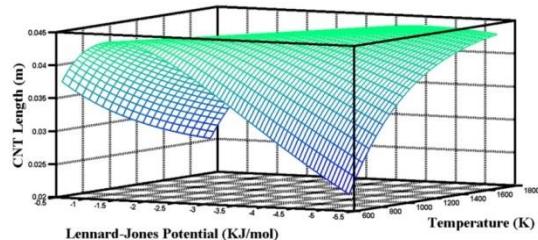


Fig. 3. Dependence of temperature and catalyst type on growth of ultra-long CNT

Figure 3 indicates that, first, there is a temperature which optimizes the growth of CNT. For example, for the growth of an ultra-long CNT with iron as MNC, the optimum temperature is about 1000 K. Similar observations were also verified by experimental works (Zheng et al., 2004; Huang et al., 2004; Moshkalyova et al., 2004; Deck and Vecchio, 2005; Chang et al., 2009). From Eqs. (5)-(8), when the temperature rises, 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 increased 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.

Second, there is an optimum Lennard-Jones potential for growth of ultra-long CNT; Van der Waals bond energy and therefore, Lennard-Jones potential 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, in 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. Existence of an optimum catalyst to optimize CNT growth has also been reported in some papers (Liu and Dahn, 2008; Liu et al., 2008; Lee and Lee, 2008).

Third, as it is observed in Fig. 3, there is only one optimum temperature for each type of catalyst. Also it shows the higher the energy, the higher the optimum temperature. Since the increase of the bond energy leads to the motion constraint on CNTs, the optimum temperature for CNT growth increases accordingly. Given a certain type of catalyst, it is therefore possible to calculate the optimum temperature for the CNT growth.

3.3. Dependence of partial pressure on growth of ultra-long CNT

Figure 4 shows the variation of CNT length versus growth time and partial pressure of decomposed hydrocarbons, based on Eq. (9) with the parameters $A_{osc}=0.77 \text{ \AA}$, $l_C=1.5 \text{ \AA}$, $d_{C-C}=1.44 \text{ \AA}$, $k_B=1.381\times 10^{-23} \text{ J/K}$, $t_{c(min)}=10^{-12} \text{ s}$, $m_C=19.926\times 10^{-27} \text{ Kg}$, $m_p=92.769\times 10^{-27} \text{ Kg}$, $N_p=40$, $\eta=1.5\times 10^{-4} \text{ s}^{-1}$, U_{LJ} (between carbon and iron) = -2.402 KJ/mol , γ (for ideal mono atomic gas)= $\frac{5}{3}$, $D=1 \text{ nm}$ and $T=973 \text{ K}$.

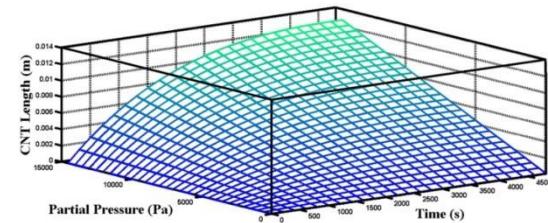


Fig. 4. Dependence of partial pressure on growth of ultra-long CNT

As it is shown in the Fig. 4, 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 (Liuet al., 2005; Puretzky et al., 2005; Wirth et al., 2009).

To investigate the relation between diameter of CNT and partial pressure, Fig. 5 is plotted which shows the variation of CNT maximum length versus partial pressure and CNT diameter with recent parameters at $t=80 \text{ min}$.

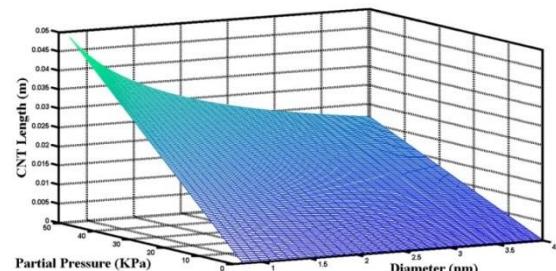


Fig. 5. Relation between CNT diameter and influence of partial pressure on growth of ultra-long CNT

Although the probability of binding increases by increasing partial pressure, for CNT with larger diameter, more carbon atoms must bond to complete a loop in CNT. Therefore, as Fig. 5 illustrates, for ultra-long CNT with smaller diameter, influence of partial pressure on CNT length is more.

4. Conclusion

The novel model presented in this paper to describe tip-growth of single CNT in CVD is based on kinetic theory of gases and longitude oscillations of metallic nanocluster on carbon nanotube (CNT) in addition to phonon vibrations of CNT on substrate. It is shown that Lennard-Jones potential can describe the interaction between CNT and catalyst quite well. Simulations demonstrate that metal nanocluster makes and keeps the carbon atoms at tip end reactive. So carbon nanotube can grow more than 1 cm. In addition, results show that carbon nanotubes with larger diameter grow less because of higher damping factors. Furthermore, effect of temperature and type of catalyst on growth is discussed and it is shown that there is an optimum temperature and an optimum catalyst for growth process. Also, it is shown that the optimum temperature is changed by using different catalysts. Finally, effect of the partial pressure of decomposed hydrocarbons on the growth is also discussed. It is demonstrated that increasing partial pressure leads to the longest CNTs and influence of partial pressure on CNTs with smaller diameter is stronger. All results from the model are in good agreement with reported experimental results and its predictions can be useful for future experimental researches.

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