**Supporting Information**

# A Mechano-Chemical Model of Growth Termination in Vertical Carbon Nanotube Forests

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***Calculation of $F_{max}$***

To calculate $F_{max}$, we used Eq. (1) [shown as Eq. (3) in the main text] as below,

$$n_{SWNT}\left|\Delta H_{rxn}\right| = \int_{h_{i,j}}^{h_{i,j}+\delta} F(x)\,dx \approx F_{\max}\delta \qquad (1)$$

To get $F_{max}$, for example, for (8,3) SWNT of 0.78 nm diameter, we followed the procedure as shown from the next paragraph and applied it to all of kinds of SWNTs as well. For the calculation of $F_{max}$ of ~3.7 nm diameter DWNTs,[11] the structural properties (e.g., $n_{SWNT}$ and $\delta$) of possible diameters inner SWNTs, which have typically 0.66 to 0.82 nm diameters less than[40,41] the outer one (~3.7 nm), were taken into account as well as the nanotube of possible outer diameters (~3.7 nm). For example, for (47,1) DWNT of 3.72 nm outer diameter, most of the possible pairs of [{(*n*,*m*), inner diameter}] = [{(38,0), 2.97 nm}, {(39,0), 3.06 nm}, {(37,1), 2.94 nm}, {(38,1), 3.02 nm}, {(36,2), 2.90 nm}, {(37,2), 2.98 nm}, {(38,2), 3.06 nm}, {(36,3), 2.94 nm}, {(37,3), 3.02 nm}, {(35,4), 2.91 nm}, {(36,4), 2.99 nm}, {(37,4), 3.07 nm}, {(35,5), 2.96 nm}, {(36,5), 3.04 nm}, {(34,6), 2.93 nm}, {(35,6), 3.00 nm}] were considered, in addition to the (47,1) outer nanotube of 3.72 nm.

*$n_{SWNT}$ and $\delta$*

From the theory of the fundamental CNT structure,[29] the number of hexagons, *N*, per unit cell of a chiral nanotube, specified by (*n*,*m*) is calculated using the formula,

$$N = \frac{2(n^2 + nm + m^2)}{d_R} \qquad (2)$$

, where $d_R = d$ if $n - m$ is not a multiple of $3d$, or $d_R = 3d$ if $n - m$ is a multiple of $3d$, and here $d$ is the largest common divisor of $n$ and $m$. Since each hexagon in the lattice contains two carbon atoms, $n_{SWNT}$ is,

$$n_{SWNT} = 2N \tag{3}$$

For (8,3) SWNT, $n_{SWNT} = 2 \times \frac{2(8^2 + 8 \times 3 + 3^2)}{1} = 388$. Also the height of a unit cell, $\delta$, is described by,

$$\delta = \frac{\sqrt{3(n^2 + nm + m^2)}}{dR} a_0 \tag{4}$$

, where $R = 3$ if $(n - m) / 3d$ is integer and $R = 1$ otherwise, and $a_0$ is the length of the basis unit vector in the graphene honeycomb lattice, 2.461 Å.

For (8,3) SWNT, $\delta = \frac{\sqrt{3(8^2 + 8 \times 3 + 3^2)}}{1 \times 1} 2.461(angstrom) = 41.98152(angstrom)$

$\underline{\Delta H_{rxn}}$

The heat of reaction at the reaction temperature, $\Delta H_{rxn}$ (in J/mol) is,[42]

$$\Delta H_{rxn} = \Delta H_0^{\mathrm{O}} + R \int_{T_0}^{T} \frac{\Delta C_P^{\mathrm{O}}}{R} dT \tag{5}$$

, where $\Delta H_0^{\circ}$ is the heat of reaction at the reference temperature (295.15 K), $R$ is the molar gas constant, 8.314 J mol$^{-1}$ K$^{-1}$, $T$ [here we used 750 $^{o}$C (= 1023.15 K) for both SWNTs[20] and DWNTs[11]] and $T_0$ [25 $^{o}$C (= 298.15 K)] are the reaction and reference temperatures, respectively, and $\Delta C_P^{\circ}$ is the standard heat-capacity change of reaction:

$$\int_{T_0}^{T} \frac{\Delta C_P^{\circ}}{R} dT = (\Delta A)T_0(\tau - 1) + \frac{\Delta B}{2} T_0^2(\tau^2 - 1) + \frac{\Delta C}{3} T_0^3(\tau^3 - 1) + \frac{\Delta D}{T_0}\left(\frac{\tau - 1}{\tau}\right) \qquad (6)$$

, where by definition, $\tau \equiv \frac{T}{T_0}$, A, B, C, and D are the constants, and $\Delta A \equiv \sum_i \nu_i A_i$ with analogous definitions for $\Delta B$, $\Delta C$, and $\Delta D$, where the $\nu_i$ with their accompanying signs are called stoichiometric numbers. The sign convention is as follows: positive (+) for products and negative (−) for reactants.

For $C_2H_2$ that used for the SWNT growth and regarded as actual feedstock,[20,30] if we assume that the dissociation reaction is, $C_2H_2 \rightarrow 2C + H_2$ and the parameters in Eq. (6) are based on the constants of the heat capacities of the ideal gas, evaluation of the parameters is as follows.[42]

| $i$ | $n_i$ | $A$ | $10^3\ B$ | $10^6\ C$ | $10^{-5}\ D$ |
|---|---|---|---|---|---|
| $C_2H_2$ | −1 | 6.132 | 1.952 | 0 | −1.299 |
| C | 2 | 1.771 | 0.771 | 0 | −0.867 |
| $H_2$ | 1 | 3.249 | 0.422 | 0 | 0.083 |

$\Delta A = (-1)(6.132) + (2)(1.771) + (1)(3.249) = 0.659$

$\Delta B = ((-1)(1.952) + (2)(0.771) + (1)(0.422)) \times 10^{-3} = 1.2 \times 10^{-5}$

$\Delta C = 0$

$\Delta D = ((-1)(-1.299) + (2)(-0.867) + (1)(0.083)) \times 10^{5} = -35200$

$\tau = T / T_0 = 1023.15/298.15 = 3.4317,$

Thus $\int_{T_0}^{T} \frac{\Delta C_P^{O}}{R} dT =$

$(0.659 \times 298.15 \times (3.4317 - 1)) + ((0.000012/2) \times (298.15^2 \times (3.4317^2 - 1))) + ((0/3) \times (298.15^3 \times (3.4317^3 - 1))) + ((-35200/298.15) \times ((3.4317 - 1)/3.4317)) = 399.8721$

Therefore, $\Delta H_{rxn} = -227480 + 8.414(399.8721) = -224115$ J mol$^{-1}$.

$\underline{F_{max}}$

For (8,3) SWNT, $F_{max}$ is,

$$F_{\max} = \frac{n_{SWNT}\left|\Delta H_{rxn}\right|}{\delta} = \frac{388 \times (-224115) J/mol}{41.98152 angstrom} \times \frac{1 mol}{6.023 \times 10^{23}} \times \frac{1 angstrom}{10^{-10} m} = 3.439 \times 10^{-8} N$$

$\cong \underline{34nN}$

***The van der Waals (VDW) interaction between two identical, parallel nanotubes***

Following the equation of the continuum model[34] that mentioned in the main text, the surface integral can be simplified by,

$$\phi(R) = \frac{3\pi\sigma^2}{8r^3}(-AI_A + \frac{21BI_B}{32r^6}) \quad (7)$$

, where $R$ is the perpendicular distance between nanotube centers, $\phi(R)$ is the potential energy of interaction per unit length, $r$ is the radius of nanotube, and $A$ (15.2 eV·Å) and $B$ ($24.1\times10^3$ eV·Å)is the Lennard-Jones (LJ) constants for graphene−graphene system, and

$$I_A = \int_0^{2\pi}\int_0^{2\pi}[(\cos\theta_2 - \cos\theta_1)^2 + (\sin\theta_2 - \sin\theta_1 + R')^2]^{-2.5}\,d\theta_1 d\theta_2 \quad (8)$$

$$I_B = \int_0^{2\pi}\int_0^{2\pi}[(\cos\theta_2 - \cos\theta_1)^2 + (\sin\theta_2 - \sin\theta_1 + R')^2]^{-5.5}\,d\theta_1 d\theta_2 \quad (9)$$

with $R' = R / r$. These integrals assume that the nanotubes are perfectly cylindrical and of infinite extent. The results thus apply to the nanotubes without faceting, and long enough that end effects can be neglected.

Figure S1 shows the tube-tube VDW interaction energy per unit length for SWNTs[20] and DWNTs[11] according to their interaction distances. For DWNTs, most of the possible chiralities for the 3.7 nm outmost-tube were taken into account. This VDW force values for DWNTs were calculated based on the assumption that only outer walls between neighboring two identical, parallel

nanotubes would contribute to the force, i.e., inner walls interaction, for which contributions of the nanotubes of all the possible chirality indices that could be as an inner nanotube, was not considered. Even though it is necessary to compute the overall VDW forces involving both inner and outer walls, it should be the same order of magnitude to the force between outer walls, because smaller inner diameter (larger interaction distance) at the same interaction distance (at the same diameter) yields lower attracting force as shown in Fig. S1, considering two parallel DWNT configuration. The minimum VDW energy, calculated in this work, per unit length at equilibrium interaction distance between two identical and parallel 3.7 nm DWNTs is ranged from 0.25 to 0.26 nN. These values agree well with the result (0.32 nN) from Chen *et al.* work[43], in which they consider the interaction between 4 nm DWNTs, within the same order of magnitude, in spite of our simplified assumption in this work.

**Supporting Information References**


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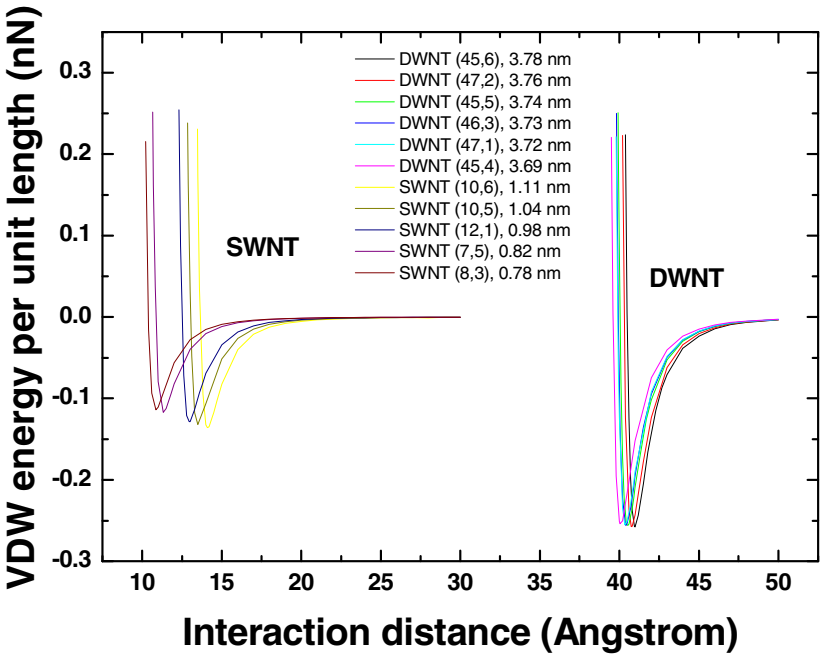


**Figure S1.** The tube-tube VDW interaction energy per unit length according to their interaction distances. Legends show the chirality indices and diameters for both SWNTs (Ref. 20) and DWNTs (Ref. 11), respectively. For DWNTs, most of the possible chiralities for the 3.7 nm outmost-tube were considered.