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Qinghong Yuan,[1] Zhiping Xu,[3] Boris Yakobson,[1,2] Feng Ding[1,2,*]

[1]*Institute of Textiles and Clothing, Hong Kong Polytechnic University, Kowloon, Hong Kong, Peoples Republic of China*
[2]*ME&MS Department, Rice University, Houston, TX77005, USA*
[3]*Department of Engineering Mechanics, Tsinghua University, Beijing 100084, Peoples Republic of China*

The energetics of topological defects (TDs) in carbon nanotubes (CNTs) and their kinetic healing during the catalytic growth are explored theoretically. Our study indicates that, with the assistance of metal catalyst, TDs formed during the addition of C atoms can be efficiently healed at the CNT-catalyst interface. Theoretically, TD-free CNT wall with 10^8-10^{11} carbon atoms is achievable, and, as a consequence, the growth of perfect CNTs up to 0.1-100 cm long is possible since the linear density of a CNT is ~100 carbon atoms/nm. In addition, the calculation shows that, among the mostly used catalysts, Fe has the highest efficiency for defect healing.

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[*] Corresponding author: tcfding@inet.polyu.edu.hk

Perfect single-walled carbon nanotube (SWCNT) has well defined atomic structure, which is depicted by a pair of chiral indexes, (n,m). Tubes with same (n,m) have identical wall structure and can be either metallic (if $n - m = 3i$, where i is an integer) or semiconducting (if $n - m = 3i + 1$ or $3i + 2$).[1] Therefore, high quality SWCNTs with same chiral indexes (n,m) are highly desired for many applications, e.g., high performance sensors and field effect transistors.

Experimentally synthesized SWCNT has a two dimensional (2D) cylindrical wall of honeycomb lattice, in which any non-six-membered ring (6MR), e.g. a pentagon, a heptagon or an octagon, should be considered as a topological defect (TD). A capped SWCNT can be viewed as an elongated fullerene and the numbers of different types of polygons in it follow:

$$\Sigma n_p(6\text{-}p) = 12, \tag{1}$$

where n_p is the number of p-membered rings (pMRs).[2] Considering only 5, 6, 7 and 8MRs, Eq. (1) can be rewritten as $n_5 - n_7 - 2n_8 = 12$. Neglecting the 12 pentagons on both caps of a SWCNT, the numbers of pMRs in a SWCNT wall satisfy:

$$n_5 - n_7 - 2n_8 = 0. \tag{2}$$

Eq. (2) indicates that an isolated non-6MRs can't appear in a SWCNT wall alone. As illustrated in Fig 1(a) and 1(b), an isolated pentagon turns a SWCNT into a sharp cone and a heptagon turns a SWCNT into a horn. In another word, TDs in a SWCNT wall must appear in the form of non-6MR clusters. Among all the potential forms of non-6MR clusters, the pentagon-heptagon pair (5|7) is the simplest one as it contains only two non-6MRs. Other forms include the 5|7/7|5 for Stone-Wales (SW) defect,[3] 7|5/5|7 for ad-dimer,[4, 5] 5|8|5 for di-vacancy,[6] contain at least 3 non-6MRs. Both previous studies and our present calculations demonstrated that 5|7 has the lowest formation energy among them[3-7] and therefore 5|7 is also the most possible form of TD in SWCNT walls.
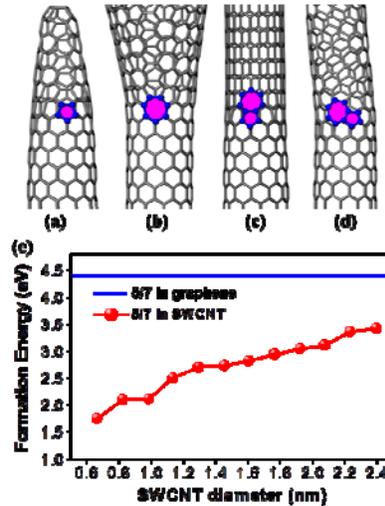
FIG 1 (Color online) An isolated pentagon turns a (10,0) SWCNT into a cone shape (a) and a heptagon turns it into a horn (b). A 5|7 that along the direction of the tube axis changes the chirality of the tube to (9,0) (c) and a 5|7 with different orientation changes the tube into a (9,1) one (d). (e), the formation energies of a 5/7 in SWCNTs vs. tube diameter (red line) and in graphene (blue line) (see [26] for details of the calculation).

It's important to note that a 5|7 is an edge dislocation core in a SWCNT wall that changes the tube's chirality.[8, 9] As shown in Fig. 1(c) and 1(d), two 5|7s with different orientations change a (10,0) SWCNT into (9,0) and (9,1), respectively. Because 5|7 is the most possible TD cluster, we conclude that *a SWCNT with single chirality along its whole wall is mostly free of any topological defect*.

At the atomic level, during the growth of a SWCNT, every polygon in a tube wall is formed at the CNT-catalyst interface by the addition of C atoms. As well documented, the incorporation of two C atoms is required to form a hexagon and the addition of a C monomer or trimer leads to the formation of pentagon or heptagon.[10, 11] Considering the C monomer, dimer and trimer have very similar formation energies on mostly used catalyst surfaces, Fe, Co and Ni,[12-15] the formation of non-6MRs during C insertion is inevitable. Thus an efficient healing of TDs is required for the growth of high quality SWCNTs.

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Experimentally, SWCNTs or few-walled CNTs up to 20 cm have been synthesized.[16-18] Signs that these CNTs have consistent chiral indexes along the wall have been observed. For example, 18 cm long SWCNTs were found to have uniformed electronic properties along the whole stem.[16] In a recent report, the electron diffraction patterns clearly revealed that a 3.5 cm long CNT stem preserves exactly same chiral indexes.[17] To maintain such a CNT perfect, in which about 10^{10} polygons existed in its wall, extremely high efficiency of defect healing that leads to a defect concentration less than 10^{-10} is required.

In this letter, the energetic stability and the kinetic healing of TDs during catalytic SWCNT growth are studied by using the density functional theory (DFT) calculations. Our study indicates that, with the assistance of the catalyst, most TDs (pentagons, heptagons and 5|7s) can be healed efficiently. At an optimum condition, the concentration of TDs can be reduced to 10^{-8}-10^{-11} and, as a consequence, the growth of 0.1-100 cm long perfect SWCNT is theoretically possible.

Firstly, let's consider the energetic requirement of growing a macroscopic perfect crystal. Under the condition of thermodynamic equilibrium, the number of defects, N_d, in a crystal is

$$N_d = N_s \exp(-\frac{E_f}{k_b T}), \qquad (3)$$

where N_s is the number of lattice sites in the crystal, k_b is the Boltzmann constant, E_f is the formation energy of the defect and T is the temperature. A 10 cm long SWCNT has ~10^{10} polygons in its wall, thus, to maintain its perfection, the number of defects must be no greater than 1 or $N_d/N_s = \exp(-E_f/(k_b \times T)) < 10^{-10}$. Under the typical CNT growth condition, $T \sim$ 800-1000 $^{\circ}$C or $k_b T \sim 0.08 - 0.1$ eV, so we have:

$$E_f > - (k_b \times T) \times \ln(10^{-10}) \sim 2.0 \text{ eV}. \qquad (4)$$

Eq. (4) is the thermodynamic requirement for the growth of macroscopic long perfect SWCNTs. As shown in Fig. 1(e), the E_f of the most energetically preferred TD unit, 5|7, in a CNT wall, fulfill Eq.(4) for $D > 1.0$ nm, where D is the tube diameter. Furthermore, the E_f of 5/7 can be as high as 4.4 eV in the graphene due to the absence of curvature energy.
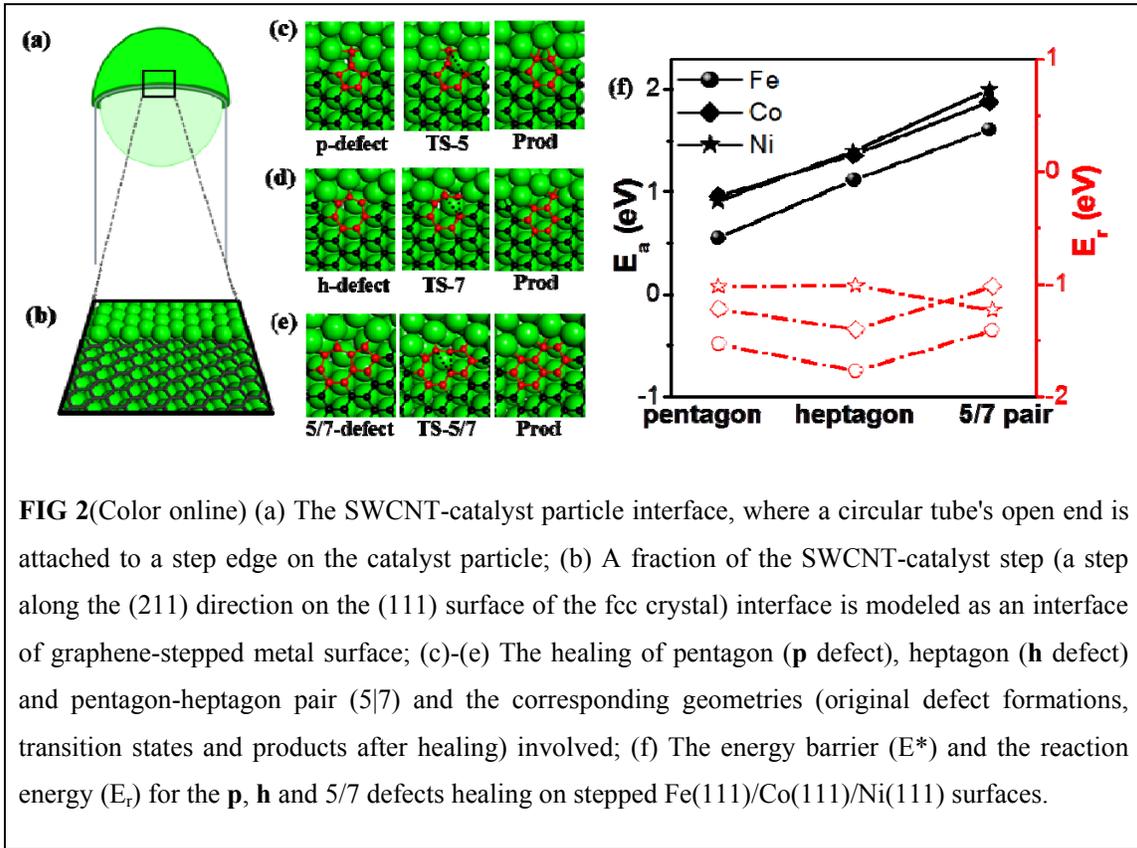
FIG 2(Color online) (a) The SWCNT-catalyst particle interface, where a circular tube's open end is attached to a step edge on the catalyst particle; (b) A fraction of the SWCNT-catalyst step (a step along the (211) direction on the (111) surface of the fcc crystal) interface is modeled as an interface of graphene-stepped metal surface; (c)-(e) The healing of pentagon (**p** defect), heptagon (**h** defect) and pentagon-heptagon pair (5|7) and the corresponding geometries (original defect formations, transition states and products after healing) involved; (f) The energy barrier (E*) and the reaction energy (E_r) for the **p**, **h** and 5/7 defects healing on stepped Fe(111)/Co(111)/Ni(111) surfaces.

Next, let's turn to the kinetics of defect healing during SWCNT growth. As well stated in literatures, the growing CNT has an open end attached to a stepped edge on a catalyst particle surface and the armchair (AC) sites are active for carbon insertion.[19-21] As shown in Fig. 2(a)-(b), an AC graphene edge attached to a stepped metal surface was adopted to model a fraction of the SWCNT-stepped catalyst interface. Such a model has been verified in previous studies of CNT growth.[19, 22] The generalized gradient approximation (GGA) with Perdew-Burke- Ernzerhof (PBE) functional (GGA/PBE) [23] was used in all calculations.

The barriers of defect healing are calculated by the climbing nudged energy band (cNEB) method incorporated in the Vienna ab initio software package (VASP)[24, 25] (details see modeling and methods of calculation in ref. [26]).

As shown in Fig. 2(c)-(2e), the healing of three typical defects, pentagons (**p**), heptagons (**h**) and their pair (5|7) are considered. As a **p** can't be healed by itself, we considered the formation of a pentagon with a dangling C atom as the initial structure (Fig. 2(c)). The healing of the **p** defect can be achieved by breaking a C-C bond and reforming another one (Fig. 2(c)). The healing of the **h** defect leads to the formation of a new hexagon with a dangling C atom (Fig. 2(d)). The 5|7 can be transformed into a pair of hexagons (6|6) by rotating a shoulder C-C bond on one side of the heptagon. Among them, as discussed before, the **p** and **h** can be frequently formed during the addition of C atoms into the growing end of a CNT. Thus, during the growth of high quality SWCNTs, the healing of **p** or **h** must be very efficient. As shown in Fig. 2(f), the barriers of **p** and **h** healing, E^*, are 0.55/0.96/0.91 and 1.12/1.36/1.40 eV on three typical catalysts, Fe/Co/Ni, respectively. Considering the typical SWCNT growth temperature, $T \sim 800\text{-}1000\ ^oC$ or $k_bT \sim 0.1$ eV, both **p** and **h** can be healed in a very short period of $\tau \sim 10^{-13} \times \exp(E^*/k_bT)$ s $= 10^{-8} - 10^{-7}$ s. So fast defect healing allows the fast growth of high quality SWCNTs.

Despite of the very fast healing of **p** and **h**, some of them can survive at a small probability. As the Euler's rule doesn't allow the existence of individual **p** or **h** in a SWCNT wall, those survived **p** or **h** must be transformed into non-6MR cluster form. Here we only consider the most possible formation, 5|7, which can be formed by the addition of a **h(p)** near a survived **p(h)**. As shown in Fig. (2e), a 5/7 pair on the edge of a SWCNT can be

transformed into two hexagons (*i.e.*, 5|7→6|6) by rotating a C-C bond. The calculated barriers of the "5|7→6|6" reaction on Fe/Co/Ni surfaces are 1.61/1.88/2.00 eV, respectively, demonstrating that the healing of 5/7 defects is more difficult than the healing of isolated **p** or **h**.

Fig. 2(f) represents the comparison of energy barrier, E^*, and reaction energy, E_r, for the healing of the three aforementioned defects on Fe, Co and Ni surfaces. Comparing with Co and Ni, defect healing on Fe surface has the lowest E^*, and E_r. This result indicates that ***Fe is the best catalyst for the growth of high quality SWCNTs***. This is in agreement with the experimental fact that Fe is the mostly used catalyst for high quality SWCNT synthesis.[18, 19, 27, 28] Thus, considering the very expensive calculations, only catalyst Fe is considered hereafter.

The above calculations revealed a high defect healing efficiency on the outmost edge of a SWCNT. During SWCNT growth, a 5|7 moves gradually into the tube wall if it is not healed on the outmost. In order to calculate the number of survived TDs in the SWCNT wall, the healing of 5|7s during its motion from the outmost front to the SWCNT wall must be considered. As shown in Fig. 3 (details can be found in ref 26), the healing of the 5|7 at different distances from the growing front can be achieved via very similar processes, namely "5|7 → 6|6". It can be seen that the barrier becomes higher and higher and the reactive energy becomes lower and lower when the 5|7 moves towards the SWCNT wall (Fig. 3). When a 5|7 is totally embedded into the hexagonal network (the 5|7-4 in Fig. 3), the barrier raises sharply to 3.22 eV, which means ***the healing of 5|7s inside the SWCNT wall during growth is nearly impossible***. Simultaneously, the reaction energy decreases from -1.5 eV on the front to

-2.5 eV in the wall, which exceeds the formation energy requirement, Eq. (4).

FIG 3 (Color online) the 5/7 defect healing during its motion from the tube front to the wall and the corresponding energy barriers (E^*) and reaction energies (E_r). Among the four steps, the 5|7 disappears in 5|7-1, -2, -3 but 5|7-4 leads to a glide of the 5|7 to the front (Details of the defect healing process in ref 23). Fe was considered as the catalyst in this study.
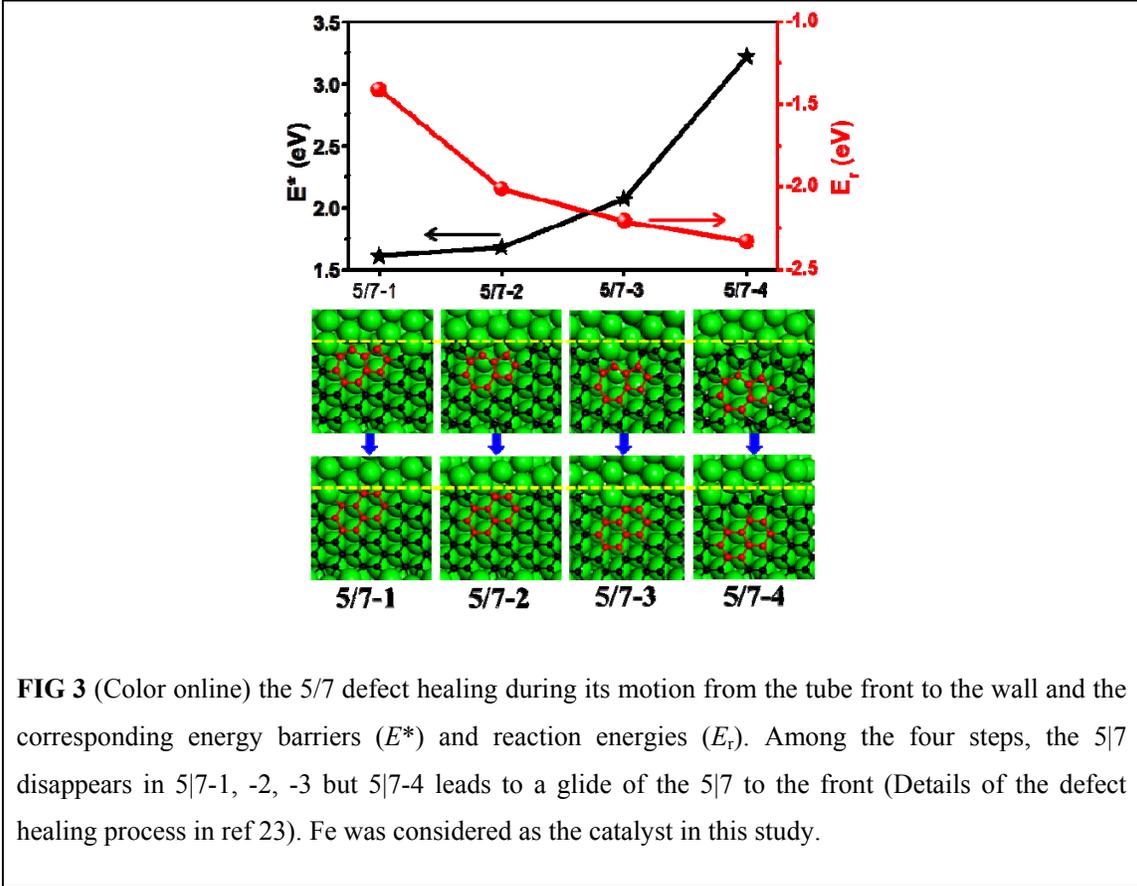
With all these barriers and reaction energies, the calculation of the TD concentration in the SWCNTs grown under a specific growth condition (*e.g.*, temperature and growth rate) is possible. As can be seen in Fig. 3, the healing of defects occurs at different depths from the front-most edge and thus the concentration of 5|7 is a function of the distance from the growing front. The time scale of defect evolution at each depth is determined by the growth rate of the CNT, $\tau = \Delta h/R$, where $\Delta h \sim 0.1$ nm is the distance between two neighboring steps and R is the CNT growth rate.

For the defect healing at each step, the concentration evolution follows

$$dC = -CK_+dt + (1 - C)K_-dt, \qquad (5)$$

where C is the concentration of the defect, $K_+ = (k_b T/h) \times \exp(- E^*/k_b T)$ and $K_- = (k_b T/h) \times \exp[- (E^* + E_r)/k_b T]$ are the reaction constants of reaction and the reverse process (*i.e.* 6|6 → 5|7) whose barrier is $E^* + E_r$. The solution of Eq(5) is

$$C = C_e + C' \times \exp\{- (k_b T/h) \times [\exp(- E_r/k_b T) + \exp(- (E_r + E^*)/k_b T)] \times t\}, \quad (6)$$

where $C_e = [1+ \exp(E_r/k_b T)]^{-1}$ is the defect concentration at thermal equilibrium ($t \rightarrow \infty$). $C' = C_0 - C_e$, in which C_0 is the defect concentration at $t = 0$.

For defects healing at the front-most (5|7-1), two types of defects, **p** and **h,** are considered and the survived **p** and **h** should be transformed into the form of 5|7 and move to the tube wall. The initial concentrations of **p** and **h**, $C(\mathbf{p})_0$ and $C(\mathbf{h})_0$, depend on the atomic details of carbon atom addition. Here we set both $C(\mathbf{p})_0$ and $C(\mathbf{h})_0$ to be 10%, which is in agreement with the molecular dynamic simulated CNT formation.[28, 29] It will be seen that, because of the low barriers of defect healing, the effect of $C(\mathbf{p})_0$ and $C(\mathbf{h})_0$ on the tube quality is negligible at most tube growth temperature ($T > 1000$ K).
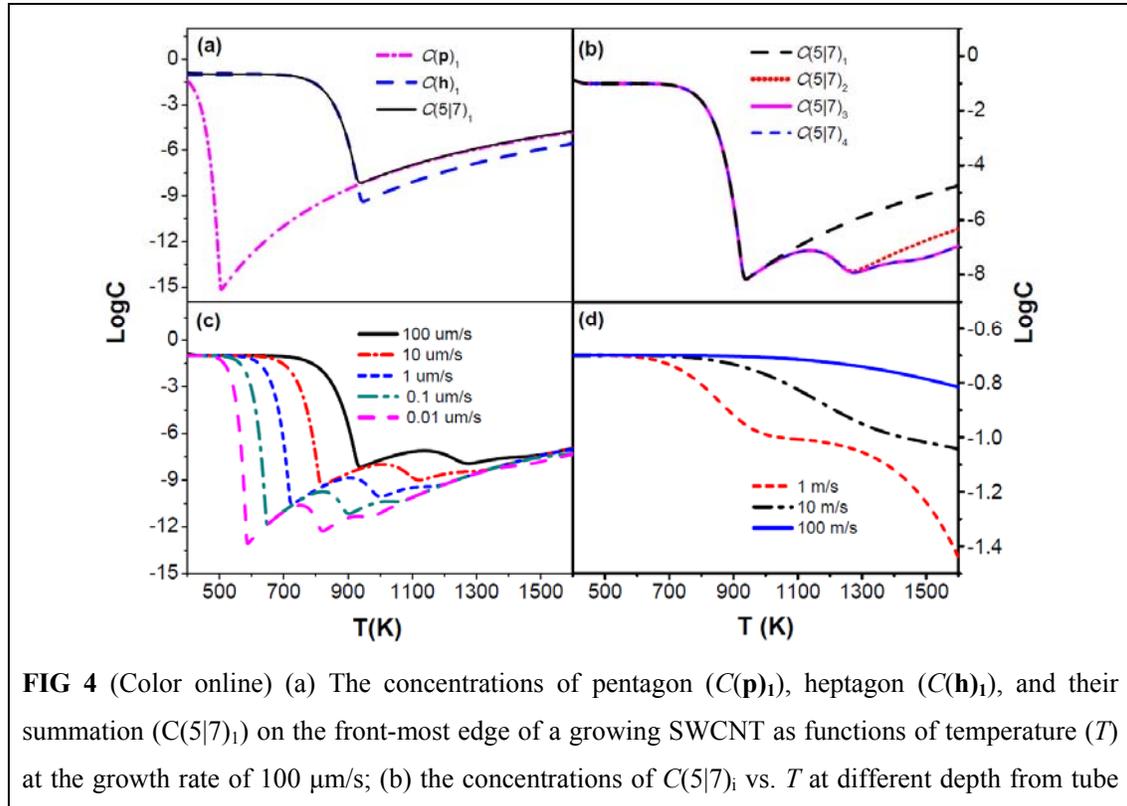
FIG 4 (Color online) (a) The concentrations of pentagon ($C(\mathbf{p})_1$), heptagon ($C(\mathbf{h})_1$), and their summation ($C(5|7)_1$) on the front-most edge of a growing SWCNT as functions of temperature (T) at the growth rate of 100 μm/s; (b) the concentrations of $C(5|7)_i$ vs. T at different depth from tube

edge at the growth rate of 100 μm/s; (c) concentrations of survived 5/7 in the CNT wall, $C(5|7)_w$ vs. T at different growth rates; (d) concentrations of survived 5/7 in the CNT wall at very fast growth rates. Fe was considered as the catalyst in this study.

Fig. 4(a) shows the concentration of pentagon ($C(\mathbf{p})_1$) and heptagon ($C(\mathbf{h})_1$) as functions of the temperature at the growth rate of $R = 100$ μm/s or $\tau = 1.0$ μs. It can be seen that the healing of $\mathbf{p}$ is very efficient and $C(\mathbf{p})_1$ is reduced to 10^{-15} at $T = 500$ K. When $T > 500$ K, the reverse processes becomes considerable and thus the $C(\mathbf{p})_1$ goes higher and higher and reaches $\sim 10^{-8}$ at $T = 1000$ K. Because of the relatively high barrier of $\mathbf{h}$ healing, the optimum healing occurs is 930 K. As we discussed before, neither $\mathbf{p}$ nor $\mathbf{h}$ defect can exist in a CNT wall along so they must be turned into 5|7 when they goes deeper from front-most edge. Thus we consider their summation, $C(5/7)_1 = C(\mathbf{p})_1 + C(\mathbf{h})_1$ as the initial concentration of 5|7 for the healing of $i = 2$.

The concentrations of 5|7 at different depths vs. temperature are shown in Figure 4(b). The local minimum of the curves at $T = 930$K corresponds to the effective healing of both $\mathbf{p}$ and $\mathbf{h}$ on the front-most. The local minimum at $T = 1280$ K in the curves of $C(5|7)_2$, $C(5|7)_3$ and $C(5|7)_4$ corresponds to the efficient 5|7 healing at the stage of $i = 2$, which barrier is the second lowest (Fig. 3). The inflection point at $T = 1500$ K corresponds the healing of defect at the stage of $i = 3$, which barrier is 2.1 eV. It can be clearly seen that the curves of $C(5|7)_3$ and $C(5|7)_4$ are nearly identical, indicating that ***there's no further defect healing if the 5|7 was surrounded with hexagons***. Therefore $C(5|7)_4$ can be regarded as the concentration of 5|7 in the tube wall, $C(5|7)_w = C(5|7)_4$.

The $C(5|7)_w$ vs. temperature with SWCNT growth rates from 10^{-2} to 10^2 μm/s are shown in Fig. 4(c). It is clear that, at any temperature, the defect concentration of a fast growing SWCNT is always higher than that of a slow growing one and all curves resemble a similar shape. So the defects can be healed more efficiently at a lower growth rate. At the growth rate

of $R = 1$ μm/s, which is a very fast experimental SWCNT growth rate,[18] the CNT defect concentration may reach 10^{-9} at an optimum temperature of ~800K or ~1100K. It should be noted that DFT calculations might underestimate the activation barrier up to 0.5 eV.[30, 31] At the temperature of CNT growth, $k_bT \sim 0.1$ eV, such an error may slow down the defect healing rate by a factor of ~ $\exp(- 0.5$ eV$/k_bT) \sim 10^{-2}$. However, in a realistic condition of SWCNT growth, in which numerous hydrogen, oxygen or water molecules involved, both the barriers and the reaction energies of defect healing can be greatly reduced. As shown in [26], the involving of a H atom or a OH group reduces the barriers and reaction energies about 60% and 20%, respectively. Beyond, the quality of a SWCNT can be further improved by low temperature growth with slow growth rate. E.g., the growth of SWCNT at 700 K with the rate of 1μm/s leads a SWCNT quality of 10^{-11}, which indicating that it is theoretically possible to grow meter long SWCNTs with a perfect walls.

Fig. 4(d) shows the 5|7 concentration vs. T at three very fast growth rates, 1, 10 and 100 nm/ns, which correspond to the SWCNT growth in classical,[32-35] tight-binding[29] and *ab initio*[36] molecular dynamic (MD) simulations. It can be clearly seen that the defects healing rarely occurs at these growth rates: only 10%, 40% and 60% defects formed during the addition of C atoms are healed. So, we can conclude that the limited simulation time is responsible for the very defective SWCNT formation observed in various MD simulations.[29, 32-36]

In conclusion, we systematically explored the concentration of the most likely formed topological defects, pentagons-heptagons pairs (5|7s), in SWCNT wall. Our calculations demonstrated that the limit of 5/7 concentration can be as low as 10^{-8}-10^{-11} and the growth of macroscopic long SWCNTs is theoretically possible. The study also shows that, relative to Co and Ni, Fe is the best catalyst for defect healing.

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