

STRONG SWNT-CATALYST ADHESION STRENGTH AS A NECESSARY CONDITION FOR SWNT GROWTH AND CHIRALITY-SELECTED SWNT GROWTH

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Carbon nanotubes (CNTs) have unique properties that make them potential candidates for many technological applications, such as nano-scale electronic devices, exceptionally strong materials, chemical sensors and hydrogen storage.¹ Intense research into the growth of CNTs over the past one and a half decades has resulted in an increase in nanotube length and yield by many orders,^{2, 3} so that CNTs of mm or cm lengths can be grown^{4, 5} and yields are close to kilograms per day. In contrast, less progress has been made in understanding the detailed CNT growth mechanism, even though this is expected to aid in identifying methods for chirality controlled production.⁶⁻¹³ In particular, it is still not understood why Fe, Co, and Ni (or alloys containing these metals) are better catalysts than other metals for growing CNTs.

Except for a few special cases such as arc discharge production of multi-walled carbon nanotubes (MWNTs)² and template growth,¹⁴ catalyst particles are essential for CNT growth. In fact, previous studies^{6, 15} show that, in the absence of catalyst particles, addition of carbon species to or thermal annealing of open SWNT ends lead to their closure. The driving force behind the nanotube closure is the instability of the carbon dangling bonds (DBs) at the open end

As illustrated in Fig. 1, carbon atoms on or in the metal particle diffuse to the open end and add into the SWNT wall (Fig. 1a). The three scenarios illustrated in the model are 1) SWNT closure ($a \rightarrow b \rightarrow c$), 2) SWNT growth without change in diameter ($a \rightarrow d$) and 3) SWNT growth where the diameter approaches that of the metal cluster ($a \rightarrow e \rightarrow f$). In scenario 1, where pentagons are incorporated at the open end, SWNT growth ceases and the nanotube may detach from the particle. In scenario 2, any defects at the SWNT end are healed, possibly by the catalyst particle, or they do not lead to a change in tube diameter (e.g., Stone-Wales type defects). Most topological defects (e.g., pentagons, heptagons or pentagon-heptagon pairs) lead to a change in SWNT diameter, and if not healed they may increase the diameter as in scenario 3. Both the second and third scenarios may be relevant for SWNT growth. For example, thin nanotubes joined to large catalyst particles are often observed in laser ablation, arc discharge and sometimes in chemical vapor deposition (CVD) with floating catalyst experiments^{7, 16} whereas nanotubes with diameters that are similar to the catalyst particles are often seen in CVD experiments of supported SWNT growth.¹⁷⁻¹⁹

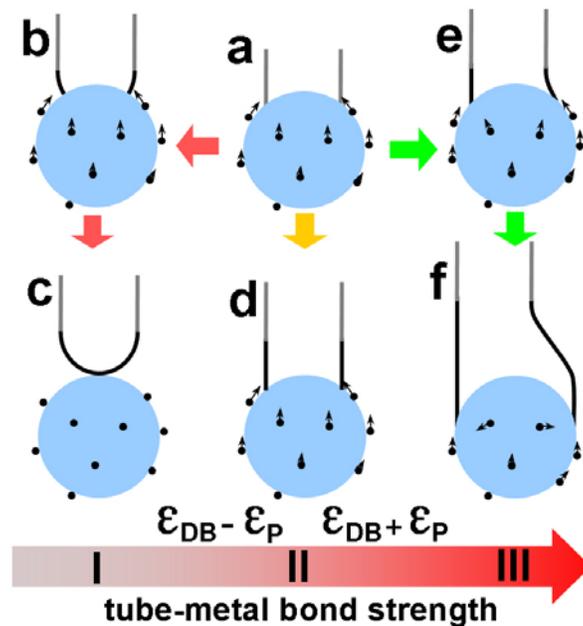


Figure 1. Three possible SWNT growth scenarios from a catalyst particle. $a \rightarrow b \rightarrow c$, the nanotube forms a closed cap; $a \rightarrow d$, the nanotube elongates without a change in diameter; $a \rightarrow e \rightarrow f$, the nanotube elongates and the diameter approaches that of the catalyst particle. The arrow shows the tube open end-catalyst interaction strength corresponding to the three growth scenarios (see text for details).

The formation energy of a SWNT open end that is bonded to a metal cluster is:

$$E_f = E_{Free} - E_{C-M} \quad (1)$$

where E_{Free} is the formation energy of DBs at the nanotube end (i.e. the energy to cut a SWNT in two) and E_{C-M} is the nanotube-metal interaction energy (i.e., the energy required to separate the open end of the SWNT from the metal cluster). Approximately,⁸ the formation energy can be written as:

$$E_f \approx n_{DB} \mathcal{E}_{DB} - n_{C-M} \mathcal{E}_{C-M} \quad (2)$$

where n_{DB} , n_{C-M} , \mathcal{E}_{DB} , \mathcal{E}_{C-M} are the number of dangling bonds, the number of carbon atoms attached to metal cluster, the DB formation energy and the carbon-metal (C-M) bond strength, respectively. For a growing tube, all carbon atoms at the open end are attached to the catalyst particle, $n_{DB}=n_{C-M}$, and:

$$E_f \approx n_{DB} (\mathcal{E}_{DB} - \mathcal{E}_{C-M}) \quad (3)$$

Eq. (3) shows the competition between the DB formation energy and the tube-metal interaction that governs which of the three growth scenarios in Fig. 1 is favored. The energetic description of the three scenarios shown in Fig 1. are:

- I. $\mathcal{E}_{DB} > \mathcal{E}_{C-M} + \mathcal{E}_p$, where \mathcal{E}_p is the penalty energy required to incorporate defects into the nanotube wall. The DB energy is larger than the sum of the C-M and penalty energies and the nanotube closes as shown in scenario 1.
- II. $|\mathcal{E}_{DB} - \mathcal{E}_{C-M}| < \mathcal{E}_p$. The DB and C-M energies are similar and their difference less than the penalty energy. There is no or very little energy gain associated with increasing or decreasing the number of carbon-metal bonds at the expense of the DBs. This favors scenario 2 and there is no change in the SWNT diameter.
- III. $\mathcal{E}_{DB} + \mathcal{E}_p < \mathcal{E}_{C-M}$. This yields negative formation energy since the C-M energy is larger than the sum of the DB and penalty energies. The adhesion energy is maximized by increasing the number of carbon-metal bonds (or number of DBs because $n_{DB}=n_{C-M}$), and the SWNT diameter will increase to that of the metal particle. This is scenario 3.

Hence, the C-M bond strength must be similar to, or larger than, the DB formation energy for SWNT growth (scenarios 2 and 3, respectively).

The validity of the model is studied by MD simulations where we artificially vary the metal-carbon bond strength from being strong, relative to the DB formation energy, to being weak. As illustrated in Fig. 2, the open end of a SWNT cap closes when artificially decreasing the carbon-metal bond strength to less that of the C-C bonds (a \rightarrow b), whereas stronger carbon-metal bonds maintain an open end that allows for SWNT growth (a \rightarrow c).

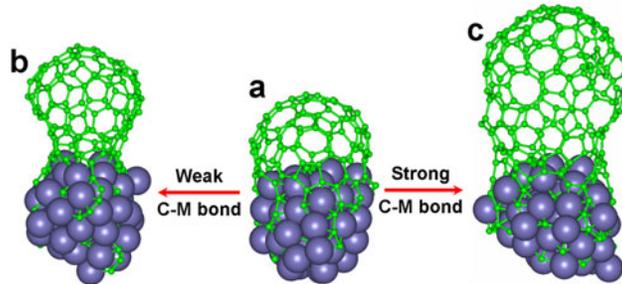


Figure 2. MD simulations of SWNT growth with varying carbon-metal interaction strengths. The open end of a carbon cap on a Fe_{50} catalyst particle (a) closes after addition of carbon atoms when the carbon-metal interaction is weak (a \rightarrow b) and remains open to support SWNT elongation when the carbon-metal interaction is strong (a \rightarrow c). The potential energy surface used to obtain the cap in panel a and the SWNT growth a \rightarrow c has previously been used to simulate the catalytic nanotube growth.^{9, 10 11 12} The carbon-metal bond strengths, which are fit to DFT energies, are stronger than the DB energies (described by the Tersoff-Brenner potential²⁰), i.e., $\mathcal{E}_{C-M} > \mathcal{E}_{DB}$.

Density functional theory (DFT) was used to calculate the formation energy of the SWNT open end and the binding strength between SWNT and metal particles. Three serious structures, (5,0) $@M_{13}$, (5,5) $@M_{55}$ and (10,0) $@M_{55}$ (M=Fe, Co, Ni, Pd, Cu or Au) was studies. The results shows

1. Fe, Co and Ni, the known efficient catalysts for SWNT growth always have stronger tube-metal

- interaction over Cu, Au and Pd, which are scarcely used to catalyze SWNT growth.
- The formation energy of the SWNT open end that attached to the catalyst particle surface are positive for Cu, Au and Pd in all cases, which means these metals can't maintain an open end of the SWNT for growth according the model presented.
 - For Fe, Co, and Ni, either the tube open end has negative formation energy (e.g. for (5,0)@M₁₃) or have very small positive value (e.g., (5,5)@M₅₅ or (10,0)@M₅₅). Combined with the penalty energy of adding defects to the SWNT wall, we can conclude that these metals are able to maintain an open end for SWNT growth.
 - There are slightly difference between the formation energy of the (5,5)@M₅₅ and (10,0)@M₅₅, which indicates the bias of the chirality during SWNT growth. The formation energy of the armchair tube is about ~0.1 eV/DB (dangling bond) lower than that of zigzag one, so the SWNT chiral distribution should be either randomly or bias to the armchair edge, which is in very good agreement with the know experimental observations.

In conclusion, a necessary condition for catalytic SWNT growth, that the binding between the catalyst particle and the SWNT end must be strong was proposed and studied by MD simulation and ab initio calculation. Based on the ab initio calculations, the bias of the chiral angle of SWNT production are revealed and the possible means of chirality selected SWNT growth are discussed.

References:

- Dresselhaus, M. S., Dresselhaus, G. & Avouris, P. Carbon nanotubes. Springer-Verlag, Berlin, Heidelberg (2001).
- Iijima, S. Helical microtubules of graphitic carbon. *Nature* 354, 56-58 (1991).
- Ebbesen, T. W. & Ajayan, P. M. Large-scale synthesis of carbon nanotubes. *Nature* 358, 220-222 (1992).
- Zheng, L. X. et al. Ultralong single-walled carbon nanotubes. *Nat. Mat.* 3, 673-676 (2004).
- Hata, K. et al. Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes. *Science* 306, 1362-1364 (2004).
- Charlier, J.-C., Vita, A. D., Blase, X. & Car, R. Microscopic growth mechanisms for carbon nanotubes. *Science* 275, 646-649 (1997).
- Gavillet, J. et al. Root growth mechanism for single-wall carbon nanotubes. *Phys. Rev. Lett.* 87, 275504 (2001).
- Fan, X. et al. Nucleation of single-walled carbon nanotubes. *Phys. Rev. Lett.* 90, 145501 (2003).
- Ding, F., Bolton, K. & Rosén, A. Nucleation and growth of single-walled carbon nanotubes: A molecular dynamics study. *J. Phys. Chem. B* 108, 17369-17377 (2004).
- Ding, F., Rosén, A. & Bolton, K. Molecular dynamics study of the catalyst particle size dependence on carbon nanotube growth. *J. Chem. Phys.* 121, 2775-2779 (2004).
- Ding, F., Rosén, A. & Bolton, K. Dependence of SWNT growth mechanism on temperature and catalyst particle size: bulk versus surface diffusion. *Carbon* 43, 2215-2217 (2005).
- Ding, F. & Bolton, K. Importance of supersaturated carbon concentrations and its distribution in catalytic metal particles for single-walled carbon nanotube nucleation. *Nanotechnology* 17, 543-548 (2006).
- Raty, J.-Y., Gygi, F. & Galli, G. Growth of carbon nanotubes on metal nanoparticles: a microscopic mechanism from ab initio molecular dynamics simulations. *Phys. Rev. Lett.* 95, 096103 (2005).
- Meng, G., Jung, Y. J., Cao, A., Vajtai, R. & Ajayan, P. M. Controlled fabrication of hierarchically branched nanopores, nanotubes, and nanowires. *PNAS* 102, 7074-7078 (2005).
- Kwon, Y.-K. et al. Morphology and Stability of Growing Multiwall Carbon Nanotubes. *Phys. Rev. Lett.* 79, 2065-2068 (1997).
- Nasibulin, A. G., Pikhitsa, P. V., Jiang, H. & Kauppinen, E. I. Correlation between catalyst particle and single-walled carbon nanotube diameters. *Carbon* 43, 2251-2257 (2005).
- Li, Y. et al. Growth of single-walled carbon nanotubes from discrete catalytic nanoparticles of various sizes. *J. Phys. Chem. B* 105, 11424-11431 (2001).
- Zhu, H. W. et al. Atomic-resolution imaging of the nucleation points of single-walled carbon nanotubes. *Small* 1, 1180-1183 (2005).
- Dai, H. et al. Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide. *Chem. Phys. Lett.* (1996).
- Brenner, D. W. Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films. *Phys. Rev. B* 42, 9458-9471 (1990).