Supporting Information

Journal: Advanced Materials

Title: Crankling Ultralong Carbon Nanotubes into Serpentes Via Landing-Controlled Process

By Yagang Yao, Xiaochuan Dai, Chaoqun Feng, Jin Zhang*, Xuelei, Liang, Li Ding,
Wonmook Choi, Jong Min Kim, Jae-Young Choi* and Zhongfan Liu*

[*] Y. G. Yao, X. C. Dai, C. Q. Feng, Prof. J. Zhang, Prof. Z. F. Liu
Beijing National Laboratory for Molecular Sciences
Key Laboratory for the Physics and Chemistry of Nanodevices
State Key Laboratory for Structural Chemistry of Unstable and Stable Species
College of Chemistry and Molecular Engineering
Peking University, Beijing 100871, P.R. China,
Tel&Fax: +86-10-6275-7157, E-mail: jinzhang@pku.edu.cn

Prof. X. L. Liang, L. Ding
Key Laboratory for the Physics and Chemistry of NanodeVices
Department of Electronics
Peking University, Beijing 100871, P.R. China

Dr. W. Choi, Dr. J. M. Kim, Dr. J. Y. Choi
Samsung Advanced Institute of Technology
San 14-1, Nongseo-Dong, Giheung-Gu, Yongin, Gyeonggi-Do 446-712, Korea

[**]Y. G. Y. and X. C. D. contributed equally to this work. This work was supported by NSFC (20673004, 20725307 and 50521201) and MOST (2006CB932701, 2006CB932403, and 2007CB936203). Y. G. Y. acknowledges Mr. X. F. Song and Mr. Y. Z. Wang from Peking University for their great help at EBL. We also thank B. Zhang, K. Yan and T. Gao for their useful discussion. Supporting Information is available online at Wiley InterScience or from the authors.
The reason to arrange slowly cooling step after growth

As reported in the literature,\textsuperscript{1, 2} CNTs are floating when they are growing and even after the carbon source is terminated. On the other hand, the CNTs can only be crankled when they are landing onto the substate, because $F_r$ is ineffective on the floating section of the CNTs. The reason to arrange slowly cooling step after growth is to make sure that the CNT grow freely to hold identical chirality along its whole length without interfering from the substate, as the common experimental condition to prepare parallel ultralong CNT arrays. After growth process is finished, the CNT is crankled controllably through letting it land onto the substate tardily and gradually. Based on this design, growth stage and crankling stage are rationally seperated. In the growth stage, ideal CNTs without defects can be reached due to the absence of disturbance. At the same time, in the crankling stage, slowly cooling experience should be valid to modulate the shape of serpentine CNTs, since nearly all CNTs are supposed to keep floating at the beginning of this stage and the crankling is considered to happen during this second process.
Figure S1. SEM (a) and AFM (b-d) images of a serpentine CNT on quartz. Small scaled Figure S1d illustrates the uniform diameter among the segments from one serpentine CNT.
Figure S2. The complete SEM image of the whole serpentine CNT, two parts of which are shown in Figure 3b. This serpentine CNT is synthesized when the angle $\theta$ is around 0°.
Figure S3. SEM images results of the experiments operated on substrates with different crystal condition. Figure S3a,b displays the serpentine CNTs grown on the substrate annealed in another muffle different from the one stated in main text. In Figure S3a, the sequential turns along the CNTs demonstrate the crankling effect from the instability of the airflow, while the absence of parallel segments denotes the lack of sufficient $F_r$, resulting from worse heat preservation performance of this muffle. The substrate in Figure S3b is cooled down slower for 15 hours after being annealed at 900 $^\circ$C for 8 hours instead of being cooled down naturally, to assist the formation of its crystal surface. In Figure S3b, a few isolated straight segments are observed within the CNTs, making us consider it as the critical condition for substrate to form serpentine CNTs. This phenomenon promotes us to correlate the worse annealing condition and less serpentine CNTs, since the only experimental condition difference between this and the experiences displayed in main text is the muffle used for annealing. To demonstrate that the lack of $F_r$ lead to the absence of parallel segments, we perform the same experience on Si/SiO$_2$ substrate, which do not have anisotropic
surface as well as the $F_r$. Figure S3c,d shows the results of such experiences with a slowly cooling step of 20 min from 975 °C to 775 °C following the growth stage. The same curves with the results provided in Figure S3a,b illustrate the absence of $F_r$ contributes to this phenomenon. This comparison substantiates that $F_r$ is one of the factors effective to influence the formation of serpentine CNTs.
Figure S4. Correlation of the lengths of parallel segments and flow flux in cooling step. When we change the flow flux during the slow cooling from 100 s.c.c.m. to 300 s.c.c.m. and 500 s.c.c.m., the distribution of lengths of parallel segments moves smaller obviously. In the histogram, green columns are related to the right scale; red and blue columns are related to the left scale.
Figure S5. Increasing length of parallel segments within one serpentine CNT from base to tip. During the landing process, \( l \) continuously decreased, leading to a continuous decrease of \( F_u \). That will increase the length of parallel segments within one serpentine CNT from base to tip. Serpentine CNT (1) and (3) are grown under 500 s.c.c.m. and serpentine CNT (2) is grown under 300 s.c.c.m..
Figure S6. Correlation of the distances between parallel segments and the tube diameters. Thicker CNTs would gain larger distances between their parallel segments due to increased $F_u$, which is proportional to $d$. 
Figure S7. SEM image of the serpentine CNT, whose $I_{ds}$-$V_g$ curve is shown in Figure 4b.
Figure S8. SEM images of the serpentine CNT, whose Raman spectra are shown in Figure 4i. The sites of mapping location 1-8 are labeled with Arabic numerals in the pictures.
Figure S9. Full Raman spectra of the one shown in Figure 4h. They are collected at 9 different sites along a serpentine CNT fabricated in a CNT-based device. The peaks at ~130 cm$^{-1}$ are the RBM peaks as they are shown in the main text and the other peaks at ~ 303 cm$^{-1}$ marked by * is from the SiO$_2$/Si substrate. Moreover, there is no more RBM peak at low frequency for thicker CNTs and high frequency for smaller CNTs. No peak located in the area marked by arrow indicates our sample does not have D-band. This demonstrates the high quality of our product.
Analysis and estimation of the shear friction force ($F_u$)

We use hydromechanics to analyze the shear friction force ($F_u$) of the floating CNT in the laminar flow of the feeding gas. According to Newton law of viscosity, the shear friction exerted on CNTs can be described as Eq. S1, where $\eta$ is the viscosity of mixed gas and $\frac{du}{dy}$ is the gradient of flow rate on the surface of CNTs. By adding the influence of the diameter of CNT ($d_{cnt}$) and the length of floating part of a CNT ($l$), we can obtain the formula of $F_u$, as shown in Eq. S2.

$$\tau = \eta \cdot \frac{du}{dy} \quad \text{S1}$$

$$F_u = \tau \cdot S_{surface} = \pi \tau l d_{cnt} \quad \text{S2}$$

To depict the flow rate distribution in the system, we build a simplified model to help estimation, which is a part of straight floating CNT located in the axis of a cylinder reaction chamber displayed in Figure S10.

![Figure S10. Schematic image of floating CNT and the reaction chamber.](image)

Through force analysis of the gas in a cylinder with a semidiameter of $y$ along the axis of chamber (the part enclosed by dashed in Figure S10), a balance between pressures, friction from the inner wall of the cylinder and friction from CNT should be formed.
\[
dp \cdot \pi \left(y^2 - r_{\text{cut}}^2\right) = 2\pi \tau, \ dy = -\pi r_{\text{cut}} \ dl \quad \text{(S3)}
\]
\[
\frac{dp}{dl} \left(y^2 - r_{\text{cut}}^2\right) = 2 \left(\tau_y, y - r_{\text{cut}} r_{\text{cut}}\right) \quad \text{(S4)}
\]
\[
\frac{dp}{dl} \left(y^2 - r_{\text{cut}}^2\right) + \tau_{\text{cut}} \frac{r_{\text{cut}}}{y} = \tau_y = \eta \frac{du}{dy} \quad \text{(S5)}
\]

Coupling with Eq. S1, we can obtain the expression of flow rate \(u\) as the function of \(y\), which is shown in Eq. S7.

\[
\int_{r_{\text{cut}}}^{y} \left(\frac{dp}{dl} \frac{y^2 - r_{\text{cut}}^2}{2y} + \tau_{\text{cut}} \frac{r_{\text{cut}}}{y}\right) \ dy = \int_{0}^{u} \eta \ du \quad \text{(S6)}
\]

\[
u = \frac{dp}{dl} \frac{y^2 - r_{\text{cut}}^2}{4\eta} - \frac{dp}{dl} \frac{r_{\text{cut}}^2}{2\eta} \ln \frac{y}{r_{\text{cut}}} + \tau_{\text{cut}} \frac{r_{\text{cut}}}{\eta} \ln \frac{y}{r_{\text{cut}}} \quad \text{(S7)}
\]

To calculate the unknown variable \(r_{\text{cut}}\) and \(\frac{dp}{dl}\), we only need two qualifications: (1) the volume flux, which is the integral of \(u\) from \(r_{\text{cut}}\) to \(r_0\), equals to 100 s.c.c.m in our standard growth condition. (shown in Eq. S8) (2) the flow rate at the inner wall of reaction chamber equals to zero. (shown in Eq. S9)

\[
\int_{r_{\text{cut}}}^{y} 2\pi y \left(\frac{dp}{dl} \frac{y^2 - r_{\text{cut}}^2}{4\eta} - \frac{dp}{dl} \frac{r_{\text{cut}}^2}{2\eta} \ln \frac{y}{r_{\text{cut}}} + \tau_{\text{cut}} \frac{r_{\text{cut}}}{\eta} \ln \frac{y}{r_{\text{cut}}}\right) \ dy = Q \quad \text{(S8)}
\]

\[
u \big|_{y=r_0} = 0 \quad \text{(S9)}
\]

To simplify Eq. S8 and Eq. S9, we get Eq. S10 and Eq. S11 as followed.

\[
\frac{dp}{dl} = Q \cdot \frac{8\eta}{\pi} \frac{\left(r_0^2 - r_{\text{cut}}^2\right)^{-1}}{\ln \frac{r_0}{r_{\text{cut}}}} \left(\frac{r_0^2 - r_{\text{cut}}^2}{\ln \frac{r_0}{r_{\text{cut}}}}\right)^{-1} \quad \text{(S10)}
\]

\[
\tau_{\text{cut}} = \frac{dp}{dl} \left(\frac{r_{\text{cut}}}{2} - \frac{r_0^2 - r_{\text{cut}}^2}{4r_{\text{cut}} \ln \frac{r_0}{r_{\text{cut}}}}\right) \quad \text{(S11)}
\]

Then introduce the values of the parameters. \(\eta\) should be the weighed average
viscosity of the gas mixture of H₂ (60%, 24.33 μP•s\(^3\)) and Ar (40%, 65.39 μP•s\(^4\)), that equals to 40.75 μP•s. Q should be 100 s.c.c.m. \(r_0\) should be 1.85 cm, which is the radium of our cylinder reaction chamber. \(r_{cnt}\) is assumed to be 1.0 nm. From these parameters, we get the solution of \(\tau_{cnt}\) and \(\frac{dp}{dl}\) as 8.028 Pa and \(-1.57 \times 10^{-3}\) Pa•m\(^{-1}\). Thus \(F_u\) can be describe as around 50•l nN, that equals to tens of pN when the length of CNT is around 1 mm. Since the van der Waals interaction energy between a CNT and amorphous SiO₂ is around 2 eV/nm,\(^5\) we can assume that the force to absorb CNT onto substrate has the same order of magnitude as hundreds of pN. Through the comparison between \(F_u\) and the absorption force, the absorption force is much larger, which indicates \(F_u\) can not drag CNT up after it has been adhered onto the substrate.

However, \(F_r\) should be the margin between the absorption force of CNT along the lattice orientation or not. Therefore we can assume that the magnitude of \(F_r\) should be one or two orders less than the absorption force and is fitly close to the magnitude of \(F_u\). Upon that we fortunately find the competition between \(F_r\) and \(F_u\) is possible and reasonable and thus reinforce our evaluation that this competition between \(F_r\) and \(F_u\) is the crucial point to determine the geometries of produced serpentine CNTs.

However we should admit that this analysis suffers from several approximations and neglects: (i) Classical aerodynamics is generally applied to analyze the system with macroscopical scales and might be inaccurate in our deduction. (ii) The model is simplified to contain only one CNT, which is easier to be calculated quantificationally. All the numerical values for the real situation should have some excursion from our estimations. (iii) The instability and fluctuation in the system are neglected in our
analysis. (iv) The margin between the absorption force of CNT along the lattice orientation or not ($F_i$) can not be estimated more accurate due to the lack of further study of the interaction between the CNTs and the anisotropic surface.
References