# Supplementary Information

The internal buckling behavior induced by growth self-restriction in vertical multi-walled carbon nanotube arrays

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Model and Critical Load of Bent Euler Beam

The standard Euler beam theory is used to calculate the load and deflection of the quasi-static straight beam. To describe and analyze the internal buckling in the CNT arrays, the relationship between the critical load of the beam and its bent shape, i.e. bent Euler beam model, must be established.

Figure 1.tif

**Figure S1** Structural model of the buckling of a carbon nanotube with independent tube assumption: (a) the model of a wave-like CNT under a force; (b) higher-mode buckling; (c) fundamental mode buckling.

**Figure S1** shows the structural model of an independent bent CNT. Under the ideal condition, a force makes an individual CNT wave-like bended, which is in an equilibrium state (as shown in **Figure S1**(a)). In a limited range, the morphology of bent CNT presents a period-like structure (as shown in **Figure S1**(b)). Here, we defined the wavelength of period as *l*, the amplitude as *D*, and the real length of a bent CNT in one period as *S*, respectively. In addition, *A* is an inflection point in a bent CNT, and *B* is the extreme point of the slope between two inflection points. Generally, we assume that *B* locates at the middle point between two inflection points.

**Figure S1**(c) is the fundamental mode buckling of a wave-like CNT. In this case, we ignored the effect of CNT gravity because it is negligible compared to the load *F*. When the beam is subject to pure bend, there is a link between the bent moment *M* and the curvature *ρ*,



Here, *E* and *I* are the Young’s module and the moment of inertia, respectively. In addition, the curvature of any point from *A* to *B* can be expressed as



In addition,



Thus, by eliminatingand *M* in the equation, and,  can be expressed as



We define that



From **Figure S1**(c), there is another equation



Thus, we can deduce an equation



Considering the boundary conditions, when, and, *k* can be expressed as



whereand. Here, α is the angle between the tangent line of *B* and the *z* axis. To calculate the stress at *B*, we utilized another equation,



It is equal to the integral of equation. Combining equations and, and eliminating *k*, the value of *p* representing the buckling in a bent CNT was obtained. Substituting all of the parameters into equation and, we can estimate the load at *B*. According to equation and, the critical value of *F* at point *B* depends on *D* and *S*. When *D* equals to zero, i.e. the CNT is quasi-straight, length *S* of individual CNT is equivalent to *l*, and the model in **Figure S1**(b) degenerates back into the primary cantilever beam model. Apparently, equation is simplified to



Here, *Fcr* is the critical load of the standard Euler beam.

图片1-s.png

**Figure S2** The bent angle *φ* at different measuring height

We assume that the CNTs at the top are quasi-straight, and their bent angles are 90° for any samples. For the same array, the bent angle *φ* decreases with measuring position closed to the substrate. Moreover, it decreases with the increase of the growth time. This phenomenon means that the curvature degree turns heavily gradually from top to bottom in an array, and it increases continuously with the increase of the growth time. This result is consistent with the analysis derived from the strain *ε*.



**Figure S3** The shift of G peak at different position in a CNT array with 15 min growth time.

The Raman spectroscopy is a tool for characterizing the change in structure caused by stress. Figure S3 is the Raman spectroscopy of a CNT array with 15 min growth time, where the interpretation is used that a G peak shift reflects the presence of stress in the CNT. A progressive shift to higher wave number of the G peak with increasing strain of the CNTs is observed.

图片3-s.png

**Figure S4** XPS data of the top of CNTs array. (a) The characteristic peaks of Fe (Fe2p1/2 and Fe2p3/2). (b) The characteristic peak of C1s.

**Figure S3** indicates that there were two elements at the top of the array. The catalyst is far from the substrate, which is the essential criterion for the top growth. There is no characteristic peak of Fe with other forms, which shows that the catalyst was protected without other valences.

Figure S5.png

**Figure S5** (a) The SEM image of a rift valley in the CNT array. The scale bar is 10 μm. (b) The back-scattering image of the links in the rift valley. The scale bar is 100 nm. (c) The SEM image corresponding to the back-scattering SEM image in **Figure S4**(b).

The rift valleys were induced by the external force, when the SEM samples were prepared. In **Figure S4**(a), there were many links in the rift valley. In **Figure S4**(b), although the intermolecular interaction was broken, the links were maintained by several nodes. The back-scattering SEM image indicates that not only carbon element exists in the nodes. In our experiment, Fe was identified. It was encapsulated in the cluster of the catalyst in the array. This phenomenon verified that the strength of this node was larger than the intermolecular interaction.

Figure s4.tif

**Figure S6** (a)The static distribution of the external diameter of the CNTs. The inset is an HR-TEM image, which shows that the number of layers is less than 10. The scale bar is 5 nm. (b) The TEM image of the dispersed CNTs. The scale bar is 1 μm.

According to **Figure S5**(a), the external diameter of the CNTs in the array is from 6 to 14 nm. The inset is a specific HR-TEM image, which shows that the external and internal diameter of CNT is about 13.45 and 7.79 nm respectively, and the number of layers is less than 10. **Figure S5**(b) shows the low-resolution TEM image. The TEM sample is from the CNTs suspended in liquid, which was prepared by ultrasound. Under the effect of ultrasound, the constraint in the array was broken. Many CNTs recovered their relaxed state, which indicates that the original internal buckling in the array was introduced by the restrictive force.