Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary material

1. Compression experiments on VACNTs

To study the buckling response of VACNT under compression, uniform compression testing was performed using Instron ElectroPuls E3000 machine at room temperature. Since the VACNTs (3mm*5mm*0.63mm) were grown on a silicon substrate, the VACNT array with the silicon substrate was placed in bottom compressive fixture, having the substrate contact with the bottom surface on the fixture. Compressive strains were applied along the longitudinal direction of the VACNTs downwards under displacements control.

All the tests were performed at the applied quasi-static loading rate of 100μm/min. The specimens were compressed to from 4.7% to 80% strain by flat platens. The actuator kept the strain for 1 min and then released the strain, allowing the specimen to recover. The compressed VACNT arrays after recovery were monitored through SEM characterization and the buckling region was imaged for each strain-increase step.

2. Van der Waals interaction between VACNTs

In order to investigate the VACNTs compression behavior, the van der Waals force between VACNTs has to be considered first. To model van der Waals interaction between VACNTs, the Lennard-Jones pair potential [1] is adopted as:

$$\varphi_{LJ} = -\frac{A}{d^6} + \frac{B}{d^{12}} \quad (1)$$

where d is the distance between the interacting atoms, A and B are attractive and repulsive constant.

The van der Waals force between two carbon atoms is derived from the above potential [2]:

$$F(d) = -\frac{\partial V_{LJ}}{\partial d} = \pi^2\sigma^2\sqrt{R}\left(\frac{35A}{64d^{4.5}} - \frac{46189B}{131072d^{10.5}}\right) \quad (2)$$

The positive value represents attractive force, while the negative value represents repulsive force.

As only the infinitesimal buckling of VACNT is considered, the force can be estimated by the Taylor expansion to the first and second terms, the higher terms can be neglected due to high order infinitesimal [2]:

$$F(d) \approx F(d_0) + \frac{\partial F(d_0)}{\partial d}(d - d_0)$$
$$= \pi^2\sigma^2\sqrt{R}\left(\frac{35A}{64d_0^{4.5}} - \frac{46189B}{131072d_0^{10.5}}\right) + \pi^2\sigma^2\sqrt{R}\left(\frac{315A}{128d_0^{5.5}} - \frac{969969B}{262144d_0^{11.5}}\right)(d - d_0) \quad (3)$$

Thus, the equivalent spring constant per unit length is:

$$K = \pi^2\sigma^2\sqrt{R}\left(\frac{315A}{128d_0^{5.5}} - \frac{969969B}{262144d_0^{11.5}}\right) \quad (4)$$

The parameters are taken as A=15evÅ^6 B=25000evÅ^{12}. To calculate buckling of VACNT with van der Waals interaction, the equivalent spring constant is used to represent van der Waals lateral support. In Figure S1, the normalized equivalent stiffness of van der Waals interaction between two CNTs decreases dramatically from 1 to almost zero as the distance between two CNT outer layers ranges from 2nm to 10nm. The mathematical results show that van der Waals interaction as lateral support is only effective when CNTs are very close to each other. Since the average distance between CNTs within bundle is around 2~3nm according to TEM characterization, the van der Waals interaction should be taken into account for buckling analysis. According to Figure S1, the nanotubes are assumed to be homogenously distributed in the forest and only the nanotubes within 5nm from the center are taken into account, including 8 in nearest layer and 16 in the second layer. The nanotubes are not in direct contact were assumed to have little effects, since the long distance and unparalleled distributed pattern lead to much less var der Waals interaction according to the paper[2]. The model only consider the effective van der Waals interaction provided by the closest surrounding nanotubes.

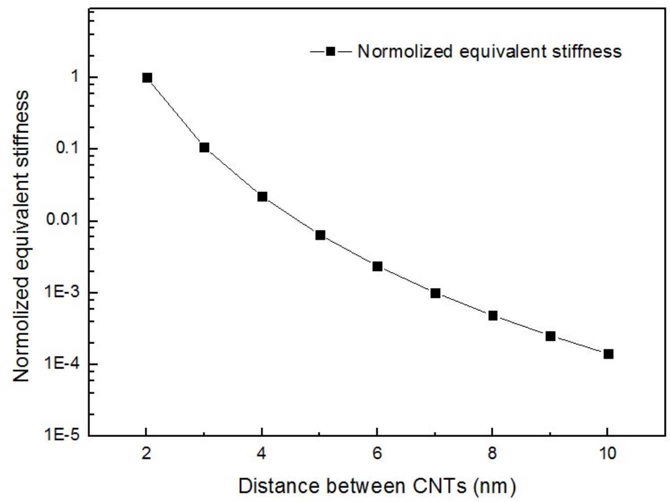

Figure S1. Normalized equivalent stiffness of van der Waals interaction with the vertical distance between two CNTs variation from 2nm to 10nm. The equivalent stiffness at 2nm is around 2.26MPa as standard equivalent stiffness.

3. CNT model with van der Waals interaction as lateral support

In this model, the interaction between inter-tubes within MWCNT is neglected, which reduces MWCNT to the equivalent VACNT column. Therefore, the VACNT is assumed to be a prismatic hollow continuum column with ring cross-section. The VACNT has hinged boundary condition in the bottom and radial constrain in the top and a concentrated force is applied at top of the VACNT.

Different to classical Euler column buckling analysis: $\sigma_{cr} = \frac{E\pi^2 r^2}{4l^2}$, this model will take the van der Waals lateral support into account. A critical buckling model with lateral support was developed by Lourie [3], which coupled the classical Euler's buckling model with an energy method. The lateral support could be converted into equivalent spring which is perfectly connected to the VACNT and provides the VACNT resistant stiffness in radial direction. In previous section, the van der Waals interactions were converted into the equivalent spring constant and thereby the VACNT buckling formula with van der Waals interaction as lateral support was obtained:

$$\sigma_{cr} = E_{CNT}(\frac{m\pi r}{L})^2/4 + \frac{K}{\pi} \cdot (\frac{L}{m\pi r})^2 \quad (5)$$

where m is the number of half waves, L and r indicate length and radius of VACNT, K is the equivalent spring constant, representing the van der Waals interaction between VACNTs.

4. Finite Element Modeling

In order to evaluate the buckling behavior of VACNT with van der Waals interaction at high aspect ratio, a model of VACNT with van der Waals interaction was developed by using finite element method. The critical buckling stress and mode were computed first. Then, the FE results were processed and the VACNT deformation shapes were extracted to evaluate the buckling response of VACNT with van der Waals interaction.

To simplify FE model, the representative volume element (RVE) for VACNT arrays was employed. In this RVE approach, the VACNT array was assumed to be homogeneously distributed and dimensions of VACNTs are uniform. Furthermore, the behaviors among VACNTs are identical due to geometrical symmetry. Lastly, the VACNTs contain the periodic unit cell in radial directions. The van der Waals interactions between VACNTs were represented by the surrounding medium support and only the VACNTs within two nearest layers were taken into account because of negligible van der Waals force in further distance according to section 3. With all of these considerations, a VACNT with surrounding support medium model was developed with properly applied boundary and interface conditions. The individual VACNT is assumed to have a unique cross-section and has perfect bond to the surrounding medium. The VACNT is assumed to be 0.63mm in length, 10nm in outer diameter and 7nm in inner diameter according to the TEM observation. The dimension of medium is 0.12*0.12*0.63mm with the VACNT in the center, so the VACNT can be considered to have infinite medium support due to large ratio between medium dimension and VACNT diameter, which is consistent with the assumption [3]. The material properties are: E_{CNT}=400GPa, v=0.3 [4].

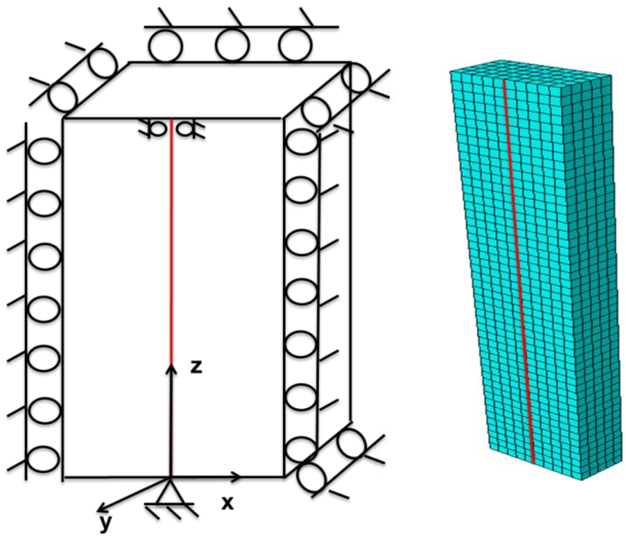

Figure S2. Schematic of boundary conditions and mesh of VACNT model with medium support in mid-cut view.

To be consistent with experiments, the VACNT in FE model is hinged in the bottom due to adhesive contact with substrate and constrained in radial direction at the top; all surrounding medium surfaces are fixed in radial directions because of geometrical symmetry. The rest parts of FE model are free. The load is compressive concentrated force applied on the top point of VACNT. In this model, 3D 2-node beam elements were used for VACNT, 3D 8-node hexagon elements were used for support medium. In order to save computational resource, the VACNT is bias mesh with 200 elements, the supporting medium part is bias mesh with 200 elements in longitudinal direction and around 240 elements in cross-section to ensure the continuity and avoid large aspect ratio elements. The analysis method is linear buckling method, which can calculate the critical buckling stress, mode and the deformation of the VACNT.

Reference

1. Girifalco, L.A. and R.A. Lad, *J. Chem. Phys.* **1956**, *25*(4) 693-697.

2. Pogorelov, E. G.; Zhbanov, A. I.; Chang, Y. C.; Yang, S. *Langmuir* **2011**, *28*(2) 1276-1282.

3. Lourie, O.; Cox, D.M.; Wagner, H.D. Phys. Rev. Lett. **1998**, *81* 1638-1641.

4. Thostenson, E., C. Li, and T. Chou, Nanocomposites in context. Composites Science and Technology, **2005**. *65*(3-4) 491-516.