Mechanics of Capillary Forming of Aligned Carbon Nanotube Assemblies

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Supporting Information

ABSTRACT: Elastocapillary self-assembly is emerging as a versatile technique to manufacture three-dimensional (3D) microstructures and complex surface textures from arrangements of micro- and nanoscale filaments. Understanding the mechanics of capillary self-assembly is essential to engineering of properties such as shape-directed actuation, anisotropic wetting and adhesion, and mechanical energy transfer and dissipation. We study elastocapillary self-assembly (herein called “capillary forming”) of carbon nanotube (CNT) microstructures, combining in situ optical imaging, micro-mechanical testing, and finite element modeling. By imaging, we identify sequential stages of liquid infiltration, evaporation, and solid shrinkage, whose kinetics relate to the size and shape of the CNT microstructure. We couple these observations with measurements of the orthotropic elastic moduli of CNT forests to understand how the dynamic of shrinkage of the vapor−liquid interface is coupled to the compression of the forest. We compare the kinetics of shrinkage to the rate of evaporation from liquid droplets having the same size and geometry. Moreover, we show that the amount of shrinkage during evaporation is governed by the ability of the CNTs to slip against one another, which can be manipulated by the deposition of thin conformal coatings on the CNTs by atomic layer deposition (ALD). This insight is confirmed by finite element modeling of pairs of CNTs as corrugated beams in contact and highlights the coupled role of elasticity and friction in shrinkage and stability of nanoporous solids. Overall, this study shows that nanoscale porosity can be tailored via the filament density and adhesion at contact points, which is important to the development of lightweight multifunctional materials.

1. INTRODUCTION

Arrays of vertical micro- and nanopillars can impart a variety of novel properties to surfaces and interfaces. For example, silicon pillars, which are typically fabricated by photolithography and deep reactive ion etching (DRIE) or metal-assisted chemical etching (MACE), can be used in batteries, photovoltaics, and hydrophobic surfaces. Micro- and nanopillars can also be used as masters for replica molding of their shapes in elastomers and epoxies. Soft high aspect ratio (AR) microstructures have a wide range of applications as dry adhesives, sensors, and actuators. Vertically aligned carbon nanotubes (VA-CNTs) are a prevalent example of an engineered surface comprising organized nanoscale filaments. VA-CNTs are synthesized by chemical vapor deposition (CVD), where individual CNTs nucleate from catalyst nanoparticles on the substrate, and then the CNTs self-organize into vertically aligned “forests.” Owing to recent advances in CNT synthesis, patterning, and post-synthesis manipulation, CNT forests can be regarded as a bottom-up complement to silicon that offers a new realm of properties and applications. For example, because of their high electrical and thermal conductivity, VA-CNTs have been used as on-chip interconnect vias and microfluids for thermal management. Because of their hierarchical porous structure, VA-CNTs have excellent dry adhesion and electrochemical energy storage properties. Over larger areas, CNT forests are promising for filtration and reinforcement of structural composites.

The interaction of filamentary surfaces with liquids is essential to their processability as well as their performance and durability during operation. During processing steps, such as cleaning or etching, capillary forces can cause closely separated high AR structures to mechanically deform, aggregate, and/or collapse. This was initially viewed as a
nuisance to high AR pillar arrays and a challenge in fabricating high AR structures. However, it has since been shown that engineering of elastocapillary interactions via the geometry, arrangement, and elastic properties enables the formation of complex hierarchical surface textures. These include dense micropillar arrays, top-gathered pyramids, helical bristle assemblies, and multidirectional lateral surface textures. In an effort to build densely packed CNT architectures with robust bulk properties, elastocapillary densification has been widely applied to both patterned and non-patterned CNT forests. “Capillary forming” is the name of the process developed by our group to fabricate a diverse library of CNT microstructure geometries by elastocapillary densification.

Previous studies of the mechanism of capillary forming of CNTs have treated CNTs as isolated vertical beams bridged by a meniscus. The magnitude of the capillary forces exerted by the meniscus spanning adjacent CNTs was compared to the stiffness of individual CNTs, and this balance was used to predict elastic CNT deformations of the CNTs and detachment from the substrate. For example, Chakrapani et al. explain the formation of ridges and voids in CNT forests by considering inhomogeneity in CNT density across the forest, which causes higher capillary pressures in denser areas. It was proposed that CNTs begin to aggregate within denser regions, and therefore, voids form in less dense regions. Liu et al. modeled the densification of individual CNT micropillars by applying a framework developed for elastocapillary aggregation of wet hair. This model predicts the minimum CNT height required to form a void-free assembly after densification, by taking into account that the hierarchical stiffening of the assembly densification proceeds upward from the substrate. Beyond a certain critical value of the CNT aggregate size, the elastic force required to deform additional CNTs to join the aggregate exceeds the capillary work output and, hence, a void is formed. A recent alternative approach used a spring-block network to simulate void formation in networks of filaments undergoing elastocapillary aggregation.

However, because CNT forests are a foam-like solid material rather than a collection of isolated beams, as assumed in previous work, it remains unclear how the collective mechanical properties of the forest influence the final organization of CNTs after elastocapillary self-assembly and forming. Moreover, this knowledge is critical to make true CNT solids and to enable engineering of the porosity of CNT solid materials by post-growth coating and infiltration. Accordingly, in this paper, we investigate how the capillary forming of CNT microstructures is governed by the wetting of the CNTs with liquid and the anisotropic mechanics of the forest under compression and shear deformation. Using a combination of in situ imaging studies, micromechanical testing, and finite element analysis (FEA), we reveal how elastocapillary forming of CNT forests is governed by the CNT forest mechanical properties and the behavior of CNT–CNT contacts.

2. KINETICS OF CAPILLARY FORMING

CNT forest microstructures (Figure 1a) were synthesized by CVD from patterned catalyst films on SiO2/Si wafer substrates. Figure 1b and Video S1 of the Supporting Information show side-view images of an individual CNT microstructure during the capillary forming process. In this experiment, liquid (acetone) was introduced by directly flooding the substrate with a 10 µL droplet far from the location of the microstructure. In all other experiments, liquid was introduced by condensation, as described in the Experimental Section.

In this case, the droplet spreads over the substrate until it reaches the CNT microstructure. Then, the acetone wets the CNT microstructure from the base, and the meniscus rises as evaporation proceeds. Notably, sometimes during infiltration, limited shrinkage is observed, typically causing the lateral dimensions of microstructures to decrease only by a few micrometers (see Figure S1 of the Supporting Information).

Capillary forming proceeds then as described earlier after evaporation from the substrate. Further, the spacing between individual CNT micropillars can affect their stability during evaporation. For example, high AR micropillars (height/diameter exceeding approximately 5:1) in close proximity can aggregate, buckle, or fold on the substrate during drying.
because of coupling of liquid menisci spanning between the micropillars. However, in this study, we focus on individual, isolated micropillars in the regime where coupling of capillary forces between structures does not influence the outcome.

To investigate the kinetics of capillary forming, a pattern of CNT microstructures having the same height, different diameters, and large spacing was imaged from the top (panels a and b of Figure 2 and Video S2 of the Supporting Information) and the liquid was delivered by condensation to prevent coupling of the microstructures by lateral capillary forces. At each time, the area of each microstructure was calculated using an edge-tracking algorithm and the diameter was determined by approximating the shape as a circle. As shown in Figure 2c, the diameter of each microstructure decreases at an increasing rate and then shrinkage slows rapidly as the diameter approaches a final stable value. During the stage of rapid shrinkage, the liquid is pinned at the outer surface of the microstructure and evaporation is causing shrinkage as the liquid—air and solid—air interfaces are coincident. After shrinkage slows, the liquid retreats within the microstructure as it continues to evaporate but the surface tension of the liquid is insufficient to cause further shrinkage. As discussed later, this can be related to the significant lateral stiffening of the CNT forest at high compressive strains. Finally, the final shape of the densified CNT forest is held by attractive van der Waals forces, which “lock” the CNTs together.

Because imaging shows that the boundary of the CNT microstructure constrains the liquid during shrinkage, we can interpret the shrinkage kinetics using classical models of droplet evaporation. However, because analytical derivation of shrinkage kinetics for arbitrary shapes is not possible, we present only limiting cases of low and high AR microstructures as spherical cap and cylindrical droplets, respectively.

We now consider a model of a drying droplet.41 The model states that the contact angle of the droplet on the substrate remains constant during evaporation, while the evaporation rate is limited by diffusion. The droplet diameter is

\[
d(t) = \alpha(t_0 - t)^\beta
\]

where \(d\) is the diameter of the droplet, \(\alpha\) is a constant of proportionality depending upon the thermodynamic conditions of the droplet, including pressure and temperature, \(t\) is the elapsed time, \(t_0\) is the time at which the droplet has evaporated completely, and \(\beta\) depends upon the surface geometry. For a spherical droplet, \(\beta = 0.5.42\) This model is appropriate for low AR CNT microstructures \((h \leq d)\), where both the top and sidewalls contribute significantly to the total evaporation rate.

For higher AR microstructures \((h > d)\) in this experiment, \(d = 0.45\) and \(0.36\) mm for \(h = 1\) mm. Here, the shape of the constrained liquid volume is more accurately represented as an evaporating cylinder. As a lower bound estimate, we consider only evaporation from the sidewalls, in which case the total area can be modeled as a flat surface undergoing diffusion-limited evaporation. Starting from first principles, the evaporation rate \((dm/dt)\) is a linear function of the area of the droplet and the concentration gradient of acetone vapor outside the droplet is assumed to be linear; i.e., \(\beta = 1\). This model captures the evaporation rate (the slope of the straight line) at the beginning of the evaporation but does not accurately predict the evaporation time \(t_0\). We found that the best fit to the evaporation from cylindrical structures with \(d/h \leq 0.5\) is using \(\beta = 0.18\), as shown in Figure 2c. This empirical model accurately described \(t_0\), the initial slope of the curve (evaporation rate), and the change in the evaporation rate as the diameter decreases until the shrinkage slows because of the densification of the CNTs.

Therefore, by comparing the measured shrinkage kinetics to both the spherical and cylindrical models, we rationalize why higher AR CNT microstructures initially start at the same evaporation rate as low AR structures, and then the rate is increased until solid—liquid separation occurs. We believe this is represented by the departure point in the measured diameter—time curves, which is close to the time at which the measurement curves depart from the appropriate evaporation model. After this instant, the evaporation rate cannot be predicted, because the liquid volume only partially fills the microstructure.

Finally, after evaporation is complete, a small amount of spring-back expansion is observed; this is more apparent on small diameter microstructures, as shown in Video S1 of the Supporting Information. However, the high remnant strain...
after evaporation is maintained by van der Waals between the CNTs, which are increased when the CNTs are brought into contact by the capillary forming process.

3. INTERNAL STRUCTURE AND ANISOTROPIC MECHANICS OF CNT FORESTS

Capillary forming is governed by coupling between the evaporating liquid and the CNT forest mechanics, which, in turn, depend upon the diameter, density, and interconnection of the CNTs within the forest. As shown in Figure 3, as-grown CNT forests have a low-density network-like morphology characterized by bends and entanglements along with the general vertical orientation of the CNTs. The CNT forests studied here have an average CNT diameter of 10−12 nm, with an areal density of approximately 200 CNTs/μm², corresponding to a mass density of ∼0.025 mg/mm³.16

As shown in Figure 1 and noted in the previous section, the CNT microstructures shrink laterally as evaporation occurs from their outer surface, indicating that the anisotropy of the CNT forest plays an important role in the capillary forming process. Additionally, the CNTs are constrained at the top, having a “crust” layer representing the early stage of growth, where the CNTs first grow in random directions before reaching sufficient density for vertically aligned growth,43,44 and at the bottom, where the CNTs are constrained because of the adhesion to the substrate. As discussed earlier and in previous work, both of these features influence the local and global balance of elastic and capillary forces and control the formation of voids within the forest.34

To quantify how the mechanics of the CNT forest influence capillary forming, we consider a CNT forest to be a transversely isotropic material characterized by transverse ($E_T$, perpendicular to the CNT alignment) and longitudinal ($E_L$, parallel to the CNT alignment) normal moduli and a shear modulus ($G'$). Because of the vertical alignment of the CNTs, $E_L \gg E_T$. Friction, van der Waals interactions, and the mechanical entanglement among CNTs are responsible for shear resistance of the CNT forest.

We first characterized the force-displacement behavior of CNT microstructures in the lateral direction, perpendicular to the average direction of the CNTs. To enable this measurement, as-grown CNT lines (width of 150 μm) were gently rolled from the vertical to horizontal orientation using a small metal pin.35 This process reoriented the CNTs parallel to the substrate without affecting their relative alignment or internal structure. After reorientation, the CNT forests were compressed perpendicular to their alignment using a nanoindentor fitted with a 100 μm diameter flat cylindrical diamond tip, as shown in Figure 4a. Compression tests were performed to strain values $\varepsilon_{\text{max}} = 0.55, 0.80, \text{and } 0.95$. The stress−strain curve of the CNT forest during lateral loading is initially linear with a very small slope, followed by an upward concave trend. Therefore, the stiffness increases significantly with increasing strain, as compression proceeds. This behavior is commonly seen in compression of open cell foams, where the plateau corresponds to deformation of cell

![Figure 3](image1.png)

**Figure 3.** Internal structure of pristine vertically aligned CNTs. (a) SEM images and (b) schematics showing the structural organization at the nanoscale.

![Figure 4](image2.png)

**Figure 4.** Interaction between CNT mechanics and liquid capillary forces. (a) Measurement of lateral stress−strain curves of horizontally aligned CNTs using nanoindentation with a flat tip, as compared to theoretical estimation (dashed line) of capillary stresses from evaporating acetone. (b) Schematic of the lateral stiffness of VA-CNTs. (c) Schematic of the lateral capillary pressure exerted on the CNTs by an evaporating liquid.

The stress−strain curve of the CNT forest during lateral loading is initially linear with a very small slope, followed by an upward concave trend. Therefore, the stiffness increases significantly with increasing strain, as compression proceeds. This behavior is commonly seen in compression of open cell foams, where the plateau corresponds to deformation of cell
walls and the upward trend at high strains corresponds to the self-contact of cell walls. The formation of new CNT–CNT contacts is therefore analogous to the self-contact of cell walls. Elastic strain recovery of approximately 2–5% is observed upon unloading, and the majority of the strain is retained by the material because of strong van der Waals forces acting on the newly formed contact regions among the CNTs.

On the basis of this nonlinear mechanical behavior, we hypothesized that the amount of densification is limited by the stiffening of the CNT forest as shrinkage occurs in the lateral direction. To explain this, we consider a section of unit length from a long CNT microstructure. As the liquid begins to evaporate, the liquid–air boundary shrinks. Because of the surface tension at this boundary, the liquid remains pinned to the outer surface of the CNT microstructure, therefore causing the CNT structure to shrink such that its volume remains the same as the remaining liquid. In this one-dimensional model, the surface tension force exerted by shrinkage of the liquid is balanced by the lateral stiffness of the CNT microstructures. This is depicted in panels b and c of Figure 4. Considering an ideal model of the CNTs as equally spaced rods, we can estimate the average compressive stress ($\sigma_c$) exerted on the sidewall of the CNT microstructure by the surface tension of the liquid

$$\sigma_c = \frac{2\gamma N}{1 - \varepsilon}$$

(2)

where $\gamma$ is the surface tension of the liquid (acetone, 25 mN/m), $N$ is the linear density of CNTs per length of edge before densification (~14 CNTs/µm), and $\varepsilon$ is the induced strain. As shrinkage proceeds, we estimate that the capillary-induced stress increases from 0.7 to 4.0 MPa, as indicated by the dashed line in Figure 4a. Therefore, by comparing the surface tension stress to the lateral stress required to further compress the CNT forest, we estimate the limit of capillary forming. This is denoted by the intersection of the solid and dashed curves in Figure 4a. At this amount of strain, shrinkage cannot proceed further because the incremental increase in capillary stress becomes lower than the increase in force needed to incrementally compress the CNT forest. Comparing this model to the measured lateral stress–strain curve predicts 0.94 capillary forming strain, as indicated by the intersection point in Figure 4a, which is close to 11-fold densification observed, for example, in Figure 1.

Moreover, because the slope of the stress–strain curve is very large at extreme strains (e.g., $\varepsilon = 0.9$), using a liquid with significantly higher surface tension will not appreciably increase the amount of densification of the CNT forest. This is shown using other values of surface tension and contact angles in Figure S2 of the Supporting Information. Therefore, to further increase the final packing density, CNT forest growth must be engineered to enable greater compressibility, i.e., a lower slope over a larger range of displacement. This could be achieved by having straighter CNTs and/or increasing the capability of the CNTs to slide and rearrange as shrinkage occurs.

4. INFLUENCE OF CNT CONNECTIVITY ON CAPILLARY MECHANICS

Because CNT contacts give rise to the nonlinear stress–strain behavior of CNT forests under lateral compression, we next studied how coating the CNTs would affect the capillary forming process. This is of further interest because surface modification can be used to tune and enhance the properties of CNT forests, including mechanical properties. Our goal was to use very thin conformal coatings to increase the density of contacts within the CNT forest, as illustrated in Figure 5a.47,48

![Figure 5. Manipulation of capillary forming via conformal coating of the CNTs with Al₂O₃ by ALD. (a) Schematics showing the thin conformal coating and their effect on causing slip resistance at CNT junctions. (b) CNT microwell patterns after capillary forming, which were first coated with 5, 10, and 15 Å of Al₂O₃. (c) SEM images showing changes in the nanoscale structure of the forest as a result of ALD coating after capillary forming.](image)

To do so, CNT forest microstructures were coated with Al₂O₃ by atomic layer deposition (ALD), as shown in panels b and c of Figure 5.49 ALD was chosen as the coating method because it enables deposition of very thin conformal coatings by control of the number of ALD process cycles and, therefore, delicate modification of the mechanical properties of the CNTs within the forest.

We found that even very thin ALD coatings on the CNTs caused a significant reduction in the amount of densification by capillary forming. As shown in Figure 5b, hollow cylindrical CNT microstructures exhibit very little densification, even when the CNT microstructures are coated with only 5 Å Al₂O₃ prior to capillary forming. Instead of densifying uniformly, the modified CNT microstructures exhibit internal voids similar to
The elastic modulus of as-grown CNTs was 185 MPa because we used a spherical tip. The elastic modulus of as-grown CNTs is significantly higher than the as-grown CNTs, indicating that Al₂O₃ increases the density of contact points relative to one another. Moreover, the slope during the onset of loading of the coated sample is significantly higher than the as-grown CNTs, indicating that Al₂O₃ increases the density of contact points where CNTs are more rigidly held together and resist slip relative to one another.

To measure the shear modulus of CNT microstructures, square cross-section microstructures (30 μm width and 50 μm height) were carefully removed from the substrate using a SEM-mounted micromanipulator and were laid down such that the CNTs were parallel to the substrate (see Figure S3 of the Supporting Information). These structures were tested using a 100 μm diameter flat tip by first applying a small compressive load (5 mN) to ensure good contact and then laterally moving the tip parallel to the substrate while recording the lateral load. The initial shear modulus was defined as the slope of the shear strain–strain curve. As shown in Figure 6b, we find that 15 Å Al₂O₃ increases the shear modulus by 350%. This is larger than the corresponding increase in lateral compressive stiffness (Figure 6a).

The increase in shear modulus can be attributed to Al₂O₃ deposited at contacting CNTs, thus “pinning” them together by constraining their relative slip, as schematically shown in Figure 5a. As a result, we conclude that the ability of the CNTs to slip relative to one another is prominent in determining the amount of densification during capillary forming. This is even more important for short (low AR) structures, where there is adhesion of the CNTs to the substrate and their entanglement in the “crust” at the top of the forest. These results could also explain CNT microstructures prepared by different synthesis methods, such as floating catalyst CVD densifying less, owing to their dense internal structure having more interconnections. For example, in a recent study where CNT forests were doped with boron, wetting and drying does not cause the forests to densify, which makes them reliable when used in liquid filtration. High-resolution transmission electron microscopy (TEM) images indicate that the boron doping targets the CNT intersections, thus pinning the CNTs at these junctions.

5. MODELING FRICTION AND SLIP AT CNT JUNCTIONS

Last, we find that the insights from micromechanical testing can be replicated by a finite element model of compression wavy CNTs (Figure 7a). In the simulation, we impose external lateral displacement to an individual CNT with prescribed waviness between two rigid planes and measure the stress–strain relationship. We simulate the effect of coating by increasing the stiffness of individual CNTs and by increasing the coefficient of friction between the CNTs and the contacting planes. The FEA simulation was performed using ABAQUS/Explicit software. The geometry of the wavy CNT model, shown in Figure 7a, has a fixed wavelength of 15 Å with an amplitude ranging from 0.7 to 1.0 Å. A beam element with a circular cross-section is employed to allow for large deformations of the CNT. Because of the symmetry, we
constrain the displacement of the bottom of the CNT in both the x and y directions and the top of the CNT only in the x direction. Note that the constraints are placed along the centerline of the wavy geometry. Then, a lateral displacement of up to 0.4 Å is applied to both rigid walls, representing deformation in the x direction by up to 40% strain.

Beginning with a frictionless condition where the friction coefficient \( \mu = 0 \) between CNTs, the simulated compression stress–strain curve (Figure 7b and Figure S4 of the Supporting Information) shows a nonlinear hardening effect as the CNT is compressed. The hardening effect can be understood by the increase of contact junctions during CNT compression, as shown in the schematics of Figure 7a. Then, Al\(_2\)O\(_3\) coating was considered by adding friction (\( \mu = 0.25 \) and 0.50) between the CNT and the walls. The top two curves in Figure 7b show that the hardening effect further increases with the coefficient of friction. From an energetic point view, in comparison of the results with and without friction, the area between the corresponding curves is equal to the work that the external force has to do. Specifically, the extra work comprises the frictional dissipation energy and the extra strain energy in the CNT because of the frictional constraint in the y direction. We also show that the lateral stress increases proportionally with the stiffness of the CNT; for example, as shown in Figure 7b, a 10% increase in stiffness of the CNT increases the imposed lateral stress by 20% in the same deformation. Therefore, the FEA model confirms that the presence of Al\(_2\)O\(_3\) coating can cause a significant hardening effect in the lateral compression of CNT microstructures based on the additional friction between CNTs and the increased effective stiffness of the coated CNT. These simulations can be used to predict the stress–strain behavior of CNT forests with varying waviness, stiffness, and friction and, therefore, could be used as a design tool for synthesis of desired final density and porosity via capillary forming.

6. CONCLUSION

We resolved the mechanism of capillary forming of CNT forests, which has been proposed as a means of building organized CNT microstructures and as a solution to the traditionally low density of CNT forest growth. We identified the stages of capillary-induced shrinkage of CNT microstructures, where the liquid first infiltrates the porous material driven by capillary forces while inducing small deformation in the material structure. Then, liquid surrounding the porous microstructures evaporates, and finally, shrinkage proceeds as the liquid evaporates according to the kinetics of a freely evaporating droplet. The densification occurs primarily in the lateral directions, because of the anisotropic mechanical stiffness of the CNT assembly. The role of the lateral compliance is demonstrated by coating the CNTs with thin Al\(_2\)O\(_3\) (<15 Å) using ALD, which prevents densification by anchoring the CNTs at contact points within the forest, thus increasing the shear modulus of the forest. This finding is confirmed by finite element simulation of lateral compression of wavy nanotubes against a barrier with variable contact friction. Considering CNTs to be an example of many nanoscale filamentary materials, this study also has implications for the design of filamentary surfaces and membranes. This is important for applications, such as biosensing and filtration, which often involve wicking and transport of liquids, as well as the design of lightweight porous materials with nanoscale architecture.

### EXPERIMENTAL SECTION

CNT Fabrication and Capillary Forming. VA-CNT microstructures were grown from a supported catalyst film (10 nm of Al\(_2\)O\(_3\) beneath 1 nm of Fe), which was deposited by sputtering onto a silicon wafer. The film was patterned using photolithography and lift-off by sonication in acetone. CNT synthesis was performed in a 1 in. tube furnace at 775 °C with ethylene (C\(_2\)H\(_4\)) as the carbon source. The recipe starts by annealing the catalyst-coated substrate to form nanoparticles, in a flow of 0.4:0.1 L/min of H\(_2\)/He. While maintaining this flow, the furnace is heated to 775 °C for 10 min and then held for 10 min more. During the growth step, a gas mixture of 0.4:0.1:0.1 L/min of He/H\(_2\)/C\(_2\)H\(_4\) leads to a growth rate of ∼1 μm/s of the CNT forests.

Unless otherwise indicated, post-growth capillary forming is performed by inverting the substrate (∼1 x 1 cm\(^2\)) over a beaker containing boiling acetone for a few seconds inside a chemical hood. The acetone exposure time is chosen in order not to cause pooling of acetone on the substrate, especially for small high AR microstructures. The diameter of the microstructures is typically reduced by a factor of 3−3.5, corresponding to ~9−12-fold densification, which is defined as the ratio between the initial cross-sectional area of the CNT micropillars and the final cross-sectional area after capillary forming. Exemplary CNT microstructures are shown before and after capillary forming in Figure 1a.

![Figure 7. FEA of the mechanics of compression of individual wavy CNTs against a rigid barrier. (a) Shapes before and after deformation, corresponding to 20 and 40% strains. (b) Stress–strain curves of the model shown in panel a with different values of Young’s modulus and coefficient of friction between the CNT and barrier.](image-url)
In Situ Videos and Image Analysis. The videos were captured using a Sony camcorder (HDR-CX700 V) using a 32-doper macro lens (Raynox MSN 505), resulting in 5 μm square pixel size at 60 frames per second time resolution. The droplet was dispersed as explained previously. The time-dependent area of each micropillar was determined by particle tracking using ImageJ.

Supporting Information

Capillary forming imaged in situ using three-dimensional (3D) confocal microscopy (Figure S1), experimental measurement of lateral compression stress–strain curves of horizontally aligned CNTs using nanoindentation (Figure S2), CNT microstructures used for shear testing, shown before manipulation (Figure S3), non-smoothed FEA trends showing the mechanics of compression of individual wavy CNTs with different stiffness and coefficient of friction (Figure S4), and Videos S1 and S2. Videos S1 and S2 show the side and top-down views respectively of VA-CNT microstructures on a silicon substrate during the various stages of capillary forming, including acetone wetting, evaporation and CNT shrinkage. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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References

19. Kordas, K.; Toth, G.; Moilanen, P.; Kumpumaki, M.; Vahakangas, J.; Uusimaki, A.; Vajtai, R.; Aizenberg, A. P. M. Chip cooling and coeﬃcient of friction.(Figure S3), non-smoothed FEA trends showing the mechanics of compression of individual wavy CNTs with different stiffness and coefficient of friction (Figure S4), and Videos S1 and S2. Videos S1 and S2 show the side and top-down views respectively of VA-CNT microstructures on a silicon substrate during the various stages of capillary forming, including acetone wetting, evaporation and CNT shrinkage. This material is available free of charge via the Internet at http://pubs.acs.org.


Supporting Information

Figure S1. Capillary forming imaged in situ using 3-D confocal microscopy. Left: SEM images showing snapshots of the shrinkage of a rectangular shaped CNT microstructure (slice near top). Right: The change in microstructure width Vs. time. Note that there is an initial shrinkage during solvent infiltration of about 10 μm, followed by 200s of solvent evaporation from the substrate, and finally the shrinkage and solvent evaporation from within the CNTs.
Figure S2. Experimental measurement of lateral compression stress-strain curves of horizontally aligned CNTs using nanoindentation; compared to theoretical estimation (dashed) of capillary stresses from evaporating acetone (CNT-acetone contact angle CA =5°), water (with CNT-water CA =5°), and water (with CNT-water CA =70°).
Figure S3. CNT microstructures used for shear testing, shown before manipulation. These microstructures were re-oriented using a micromanipulator to become horizontally aligned on their side, with the CNTs parallel to the substrate.
Figure S4. Non-smoothed Finite Element Analysis (FEA) trends showing the mechanics of compression of individual wavy nanotubes with different stiffness and coefficient of friction.