In situ Mechanical Testing Reveals Periodic Buckle Nucleation and Propagation in Carbon Nanotube Bundles

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1. Introduction

The study of carbon nanotube (CNT) foams, bundles, forests, carpets, and turfs in photolithographically defined patterns has received an increasing amount of attention due to their unique thermal,[1] electronic,[2] light trapping,[3] and mechanical[1,4,5] properties, and as lucrative candidates for their applications in contact thermal switches,[1] cold cathodes,[2] and low-reflectance coatings.[3] As structural thin films, CNT foams have also shown promise for energy dissipation and cushioning applications.[4,6] However, no comprehensive studies addressing their collective mechanical behavior have been reported. A thorough understanding of the mechanical response of CNT-based structures to deformation will provide insight into their lifetime and durability, develop a basis for potential new applications, and shed further light on the fundamental deformation processes operating in these multiscale systems.

While much work has been done to study the unique properties of individual CNTs and CNT-embedded materials, only a few reports addressing mechanical deformation of CNT foams exist.[1,4,5,7–9] Yet CNT foams exhibit intriguing structural behavior, with some achieving nearly full recovery from large strains under uniaxial and cyclic loading,[9] while others display permanent deformation under only moderate strains.[1] Interestingly, in both cases, the post-compression scanning electron microscopy (SEM) images indicate coordinated buckling, evidenced by wavy surface morphology, with buckling appearing to be initiated preferentially from the substrate, regardless of whether the CNTs remain attached to it or not in the course of deformation.[4] Nanoindentation tests on CNT foam films[9,10] and on photolithographically defined features[1,8] have provided tangent and elastic moduli, but they cannot explore this wrinkle-like morphology due to its highly localized and limited total strain. In addition, specific CNT growth conditions appear to result in significant differences in the mechanical behavior of the generated structures, as evidenced by a wide range of reported elastic moduli (15–100 MPa).[1,8,9] Some of this variability has been addressed qualitatively in terms of the visible differences in foam morphology by McCarter et al.[8] Here we present the results of mechanical deformation and ensuing morphological evolution observed in cylindrical, 50-μm-diameter CNT foam bundles subjected to uniaxial compression under different strain rates.

2. Results and Discussion

The cylindrical “bundles” studied in this report are composed of nominally vertical, interwoven CNTs displaying gradients in both density and tube alignment in the direction of growth. In referring to these CNT agglomerates as foams, we are drawing an analogy to the characteristic microstructures of foams, cells, and struts in cellular materials, and the relatively well-understood mechanisms behind their mechanical response to deformation, which provides a useful characterization framework.

In order to elucidate the deformation mechanisms operating in CNT foams under mechanical loads, we perform uniaxial micro-compression experiments on cylindrical CNT foam bundles, or pillars, with diameters of 50 μm and heights of 61–68 μm attached to Si substrates. Load versus displacement data is gathered in a
nanoindenter equipped with a custom-machined diamond flat punch tip, as well as in a custom-made in situ mechanical deformation instrument, SEMentor\textsuperscript{[11]} (described in Subsection 2.2.2). Utilizing the reported procedures to properly account for instrumental attributes\textsuperscript{[12–14]} in order to deconvolute the specimen-only load–displacement data from the combined machine–sample response (Section 2.1), we calculate engineering stresses and strains at various prescribed displacement rates and calculate the storage and loss stiffnesses as a function of frequency and strain (Section 2.3). Analysis of this data in combination with the morphological characterization of the post-compression pillars via SEM and in situ deformation (SE Mentor) provides a number of novel insights into the mechanical properties and deformation mechanisms involved in CNT foam compression.

2.1. Microstructural Characterization

Since the specific microstructure of CNT-based structures plays a key role in their mechanical response, we overview some characteristic morphological aspects of the CNT bundles studied here:

- Under lower magnification (~1 000×), the tubes in the bundles appear vertically aligned, that is, perpendicular to the substrate (Fig. 1, center). However, under larger magnifications (>30 000×), it becomes evident that the CNTs are randomly oriented in a very porous network, forming a fibrous, interconnected web of support structures where individual tubes interact with one another (Fig. 1, left and right). The presence of these interactions distinguishes these CNT “foams” from vertically aligned CNT forests, in which individual tubes are far enough apart to grow without physically interacting with their neighbors.
- There exists a height-dependent inhomogeneity in the bundle structure due to its growth mechanism. Lower density and less vertical alignment at the bottom results in fewer and weaker load bearing members, creating a more compliant material at the bottom. These morphology gradients are illustrated in the high magnification images taken at evenly spaced heights along a pillar in Figure 1.
- The diameters of individual multiwalled CNTs comprising the bundles are 20–50 nm as determined by transmission electron microscopy (TEM)\textsuperscript{[15]}

Determining the average tube number density has proven to be challenging due to the small size of individual pillars (lack of material) and the size of the “pores” (~200 nm). We are currently exploring nitrogen adsorption methods (Brunauer–Emmett–Teller, BET) for determining the surface area, and indirectly the volume fraction, of a continuous film of identically grown CNT foam.

2.2. Uniaxial Compression

Unlike during nanoindentation, load–displacement data obtained for uniaxial compression can be readily converted into axial engineering stress versus strain. In addition, as stated earlier, the wrinkle morphology is only visible at larger than moderate strains under uniaxial loads. Here, micro-compression experiments are performed either ex situ by using the XP module of an Agilent Nanoindenter G200 or in situ in the SEMentor.

2.2.1. Decoupling Material and Instrumental Response

Generally, the raw load–displacement data collected during nanoindentation experiments combine both the material and instrumental responses. Careful measures have to be taken in order to accurately decouple the sample-only response from the collected data by properly representing the mechanical equivalent of the entire sample–instrument system.\textsuperscript{[12,13,16]} The equivalent mechanical model of the nanoindenter used in our experiments is shown in Figure 2a. Raw load data (\(p_{\text{raw}}\)), taken by the inductive coil gauge, and raw displacement data (\(u_{\text{raw}}\), taken by the capacitive displacement gauge) are gathered continuously (250–500 Hz) throughout the test. After compressing the pillar, the indenter is held in the air at several characterization points within the raw displacement range obtained during compression to accurately determine the spring force and damping at the same place in the range of motion as the data is gathered (see Experimental). The load required to maintain these displacements is the column spring force, \(p_s\), (a result of the column spring constant, \(k_s\), in Fig. 2a), which is position-dependent over large distances (enough to result in a 0.05 mN force difference over some regions of raw displacement). The spring force is then interpolated and removed from the raw load to obtain the corrected load, \(p_{\text{corr}}\), on the indenter/load frame/sample assembly (solid boxed region of Fig. 2a). It follows that the load on the sample is simply the load on this assembly due to the fact that these three elements are in series. Finally, there is a small contribution to the force by the machine damping (\(D_m\)), which is calculated during the characterization in air. However, we find that this contribution is only marginally important for the highest strain rates (highest displacement rates, \(u\)) of 0.1 and 0.5 s\(^{-1}\) where the force, \(D_m u\), is on the order of 0.05 mN.

\[
p_{\text{corr}} = p_{\text{raw}} - p_s + D_m u
\]

(1)
The corrected displacement, that is, the actual displacement into the sample, accounts for the frame stiffness, $k_f$, and the indenter head stiffness, $k_i$:

$$u_{corr} = u - \frac{p_{corr}}{k_f} - \frac{p_{corr}}{k_i}$$

(2)

where $k_f$ for our system is $5.92 \times 10^6 \text{ N m}^{-1}$ (calculated during instrument set-up and calibration) and $k_i$ is calculated by using the known elastic modulus, $E$, and Poisson’s ratio, $\nu$, of diamond. The relationship for determining $k_i$ is\(^{(12)}\)

$$k_i = \frac{2E}{(1-\nu^2)A_c/\pi}$$

(3)

where $A_c$ is the cross-sectional area of the indenter. Both corrections turn out to be inconsequential ($\sim 0.01 \text{ nm}$) for such a compliant material under such large deformation but are included for completeness.

During each experiment, the surface contact is marked by attaining the $50 \text{ N m}^{-1}$ threshold in the user-defined harmonic contact stiffness, as a threshold any lower results in false positives for contact due to the mechanical and electrical noise. Upon establishing contact, the harmonic measurement option is turned off before proceeding with the compression due to the fact that it cannot be oscillated fast enough to provide meaningful data at the faster displacement rates. It is important to recognize that crossing this threshold represents the initial contact, likely caused by several stray tubes rather than by the full cross section; full contact usually occurs within $0.5 \text{ \textmu m}$ from that point. We identify the first attainment of full contact through post-processing, locating a tangent slope of $10 \text{ N m}^{-1}$ from the load–displacement data for a consistent surface find for all tests. This value corresponds to a visible increase in $p_{corr}$ relative to the maximum load attained in the quasi-static tests. Utilizing the correct location of the sample surface the actual load and displacement felt by the pillar is tared at that point for a zero stress–strain initial point. At the same time, $p_{corr}$ is already approximately zero at this point, being less than $0.04 \text{ mN}$ while the maximum $p_{corr}$ approaches 40 times this value.

The nanoindentor compresses the samples at a constant prescribed displacement rate, and therefore constant strain rate, throughout the entire experiment (loading and unloading). Four different nominal displacement rates were used: $\sim 65 \text{ nm s}^{-1}$, $\sim 0.65 \text{ \textmu m s}^{-1}$, $\sim 6.5 \text{ \textmu m s}^{-1}$, and $\sim 32 \text{ \textmu m s}^{-1}$, spanning just over three orders of magnitude of strain rate: 0.001, 0.01, 0.1, and 0.5 $\text{ s}^{-1}$. The prescribed displacement schedules and the instrument’s response to them are shown in Figure 2b. Note that the displacement schedules for the two slowest rates have nearly perfect control (straight lines), while the two fastest rates show a progressive decrease in control illustrating the limitations of the inherently load-controlled nanoindentor.

2.2.2. Material Response

The mechanical response of individual pillars is analyzed through uniaxial stress–strain curves, post-mortem morphology, and in situ deformation videos. Each pillar is selected for mechanical testing from an array grown through chemical vapor deposition (CVD) on a lithographically patterned substrate, as can be seen in Figure 3a (See Experimental for growth details). We chose the
50-μm diameters with the aspect ratio of 1.2–1.4 (height/diameter) because they are large enough to produce the surface undulations observed previously[1,4] and theoretically predicted,[17] while being small enough to capture the local deformation events during compression in our custom-built in situ mechanical deformation system, SEMentor.[11] SEMentor is composed of a nano-mechanical dynamic contact module (Agilent Corp.) inside an SEM chamber (Quanta 200, FEI), which allows us to simultaneously characterize the physical morphology alongside the load–displacement curve during deformation.[11] Since the SEMentor arm’s travel distance is limited to 30 μm, we were able to compress the pillars only up to about 50% strain in situ.

Engineering stress (σ) and strain (ε) were calculated using the initial diameter and height of the pillar, d₀ and h₀, respectively, along with the corrected load and displacement discussed in Subsection 2.2.1.:

\[
\sigma = \frac{p_{\text{corr}}}{\pi d_0^2/4}, \quad \varepsilon = \frac{h_{\text{corr}}}{h_0}
\]

A representative stress–strain curve (Fig. 3b) corresponding to the compression of a single foam pillar at a rate of 0.001 s⁻¹ illustrates the common features found at any measured strain rate. Utilizing the foam-like analogy, we first note three distinctive regimes: a short elastic region, followed by a plateau-like segment where the deformation is characterized by cyclical “humps” at a relatively constant global applied stress, followed by stiffening indicating the onset of densification. While occurrence of these distinct types of mechanical behavior is typical for foams and other...
certain features are specific to the CNT bundles: i) a large initial buckling event marked by a significant load drop following the initial elastic deformation regime and ii) a series of distinct humps in the plateau-like segment, corresponding to the initiation and propagation of folding/buckling events in the bundle (Fig. 3c).

Through in situ experiments, we discover that localized, periodic, bottom-to-top buckling governs bundle deformation, as illustrated by the panels taken from an in situ video (Fig. 4) at six regularly spaced strain/time intervals along the deformation curve.\(^1\) Analogously to the report by Cao et al.,\(^4\) we believe this is due to the inhomogeneity in material properties along the vertical axis. Specifically, the density gradient (lower density at the bottom) and variation in the tubes' relative vertical alignment (more aligned at the top) leads to a much more compliant material near the substrate compared to the stiffer one at the top. We observe that after the initial buckling, all subsequent buckled layers form in the following fashion: i) buckles start as a localized fold or a bulge at the pillar surface, then propagate laterally (or possibly in a spiral) through the pillar diameter (Fig. 5), ii) buckles always form in succession, with each previous (lower) buckle fully completing before the initiation of the next buckle. In addition, the entire pillar region above the buckles shows no signs of deformation, relegating all the strain accommodation to this buckling mechanism. Importantly, we observe that the wavelength of the post-compression undulations does not depend on the strain rate, as

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**Figure 4.** Frames from an in situ video [15] illustrating the bottom-to-top sequential buckling. Each frame corresponds to the numbered six points denoted in the stress–strain curve (top), taken simultaneously with the images.

**Figure 5.** Frames from an in situ video [15] illustrating the formation and propagation of a single buckle. Each of the frames aligns with the points on the accompanying stress–strain inset illustrating how a single hump corresponds to buckle initiation and propagation. The direction and magnitude of buckle propagation follow the overlaid arrows.
it remains at a relatively constant value of ~2 μm in all compressed pillars. As each 2-μm fold accommodates around 6 μm of unbuckled material, the final number of folds is simply a function of the total deformation only and thus also remains approximately constant over the strain rates and pillar geometries tested.

We find that initial buckling is always more pronounced than all successive ones. It occurs at significantly higher loads (Fig. 3b and d) and its formation can be dramatically different even at the same loading conditions, sometimes initiating an abrupt shortening of the pillar. This causes the indenter head to momentarily lose contact with the pillar top (Fig. 6), resulting in a rapid load removal, and therefore a much lower stress immediately after buckling. This loss of pillar–indenter contact is due to the pillar collapsing faster than the prescribed rate of the indenter head motion. We observed this phenomenon in several experiments at each strain rate and during compression in both the nanoindenter and the SEMentor, suggesting a physically driven mechanism for this initial collapse rather than an experimental artifact. The inset in Figure 3d shows a zoomed-in region in the stress–strain curves at each strain rate and contains three examples where the pillar “jumps” away from the indenter tip at strain rates of 0.001, 0.1, and 0.5 s⁻¹, and one example without it at the strain rate of 0.01 s⁻¹. The loops in the stress–strain data are indicative of this loss of contact. Several samples, however, do not exhibit any discrete behavior and proceed at the prescribed nominal displacement rate, as shown in Figures 4 and 5. Since these materials are highly inhomogeneous, sample variation among the pillars may be responsible for these differences.

We hypothesize that these discrete buckling events are caused by the lateral propagation of a zipping-like layer, possibly due to the attractive van der Waals forces between individual tubes, pulling them towards one another. This “zipping” layer is initiated by crossing some threshold force at the weakest point, after which it becomes more energetically favorable for the adjacent CNTs to coalesce together and buckle, propagating the condensation/buckle reaction through the entire layer. In the cases where the zipping does not occur and the indenter head stays in contact with the bundle throughout the compression, it is possible that either the applied force never reaches that needed to “zip up” enough CNTs or the critical concentration of tubes necessary for coalescence is not in place. The first buckling event may also be affected by a rigid boundary condition at the substrate, as first explored by Zbib et al., who found that this condition can result in an increased load. However, here the boundary conditions are not constant, as individual CNTs are pulled off from the substrate (Fig. 7a). Several factors could contribute to the marked difference in behavior between the initial buckle and all subsequent buckles; the catalyst-anchored CNTs can be pulled out and/or the microstructural network required for the zipping behavior is only possible at the base (i.e., the network is too ordered or too dense elsewhere). Gravity cannot be responsible for causing the undeformed region of the pillar to “fall” upon the buckled first layer as a single tube can easily bear the load of the entire pillar.

Figure 6. Frames from an in situ video [15] illustrating the sudden initial buckle formation and momentary loss of contact with 0.8 s passing between the image two images. Details of the initial buckle formation are difficult to see as they occur faster than the electron beam scan rate (0.3 μs per pixel on a 512 x 442 image, which is averaged over several scans to improve image quality). Note the gap formed between the collapsed pillar and the displacement-rate-constrained (300 nm s⁻¹) indenter head.

Figure 7. a) An SEM image of a post-mortem pillar base clearly showing several individual CNTs pulled away from the substrate surface. The initial anchor point of these tubes (the darker-to-lighter transition of the substrate) is indicated by the arrow. b) Several high-magnification SEM images reveal details of buckled regions. Within each buckle, CNTs appear to bend without fracturing. The bottom left image shows a series of buckles of approximately the same size.
Also, gravity acts in two different directions in the nanoindenter (parallel to the axis) and SEMtor (perpendicular to the axis). Additionally, CNTs within each fold do not appear to be broken (Fig. 4b), indicating energetic favorability for reconfiguration rather than structural failure during the zipping process.

While the stress–strain curves at all strain rates share foam-like features, the plateau regime humps, corresponding to individual buckling events, are noticeably dependent on strain rate. There are distinct differences in the shape of these humps, with the slower strain rates producing smooth, sinusoidal undulations and the faster rates approaching more of a sine-squared form, as evident from the typical stress–strain curves for four different strain rates plotted in Figure 3d. For all strain rates, each undulation occurs at a progressively higher load, rather than forming a true plateau, typical for cellular solids, because each global buckling sequence must nucleate and propagate through a stiffer, denser material than the previous one due to the property gradients discussed earlier. Although the curves chosen for Figure 3d appear to reach higher stresses with higher strain rate, this trend does not hold true for all sets of data, and the maximum attained stress depends on the accuracy of the initial pillar–indenter alignment and microstructural variation between individual pillars.

### 2.3. Viscoelastic Characterization

Viscoelastic materials are commonly characterized by their storage and loss moduli, where the former represents the stored energy, or elastic response, and the latter corresponds to the amount of energy dissipated as heat. Here, we calculate the storage and loss stiffnesses, \( k \), rather than moduli, \( E \), because their interdependence, via the well-known relation\[^{19}\]

\[
E = k \frac{\sqrt{\pi}}{2\beta} \frac{1 - \nu^2}{\sqrt{A}},
\]

In this relation, \( \beta \) is a constant that depends on the indenter geometry (1 for a flat punch) and \( A \) is the contact area (\( \sim 2500 \mu \text{m}^2 \)). Here, this calculation will result in the approximate relation \( E[\text{kPa}] \approx 20 \times k[\text{N/m}] \) (assuming \( \nu \approx 0.3 \)). We compute the storage and loss stiffnesses by oscillating the indenter head at \( \sim 8\text{-nm amplitude while sweeping the frequency from 1 to 45 Hz} \) at ten different constant strain values: from 0.01 to 0.8. Following the procedures and calculations described by Herbert et al.\[^{14}\] and Wright et al.,\[^{13,16}\] the storage \( (k_{\text{storage}}) \) and loss \( (k_{\text{loss}}) \) stiffnesses of

![Figure 8](https://www.MaterialsViews.com)

**Figure 8.** a) Storage and loss stiffnesses as a function of frequency gathered at three different strains (see legend). Closed symbols correspond to storage stiffness (elastic response), and open symbols represent loss stiffness (energy dissipation). b) Uniaxial compression data accompanied by an oscillatory, dynamic stiffness measurement to determine the stiffness continuously throughout the quasi-static (strain rate = 0.001 s\(^{-1}\)) test. Gray arrows illustrate the one-to-one correspondence between the features in the stress–strain and stiffness–strain curves. c) Storage stiffness as a function of frequency and strain showing high strain dependence, but little frequency dependence. d) Loss stiffness as a function of frequency and strain showing approximately equal dependence on strain and frequency. Increased strain and decreased frequency elicit maximum energy dissipation.
the entire sample/frame assembly (solid boxed region in Fig. 2a) were obtained by finding the real and complex parts, respectively, of the stiffness differences between oscillating the indenter head on the sample at a fixed position and in air at the same raw displacement.

\[ k_{\text{storage}} = \frac{F_0}{\mu_0} \cos \varphi - \frac{F_0}{\mu_{0\text{air}}} \cos \varphi_{\text{air}} \]  

(6)

\[ k_{\text{loss}} = \frac{F_0}{\mu_0} \sin \varphi - \frac{F_0}{\mu_{0\text{air}}} \sin \varphi_{\text{air}} \]  

(7)

Here \( F_0 \) and \( \mu_0 \) are the load and displacement oscillation amplitudes respectively, \( \varphi \) is the phase angle between the load and displacement oscillations, and the subscript “air” refers to the measurements taken while the head oscillated in air (i.e., not in contact with the sample). While this method treats the entire solid boxed region as a black box, these stiffnesses remain independent of the indenter mass, which is important as values calculated for the indenter head mass utilize several assumptions and can be unreliable. It is reasonable to assume that these stiffnesses correspond to those of the sample since both the frame and the unrestrained. It is reasonable to assume that these stiffnesses correspond to those of the sample since both the frame and the indenter head stiffnesses are several orders of magnitude higher than those of the sample and thus can be assumed to be infinite.[14]

The storage and loss stiffnesses obtained by utilizing this procedure are shown in Figure 8 by closed (storage) and open (loss) symbols. An alternate procedure reported by Wright et al.[13] models the sample as a standard linear solid (SLS), thereby enabling the calculation of the sample storage and loss stiffnesses for a continuous range of frequencies and accounting directly for the indenter head and frame stiffness. Following this approach, we used the frequencies of 8, 15, and 35 Hz to obtain the sample parameters \( k_1, k_2, \) and \( D_0 \) of the SLS modeled sample. We find that while of the same order of magnitude, these SLS-based predictions do not follow the trends of our calculations, strongly suggesting that CNT foams do not deform as a SLS and require the development of a more complex mechanical model.

We find that the storage stiffness is frequency-independent over the range of frequencies tested, indicating a single energy storage mechanism operating over this range. It is also ten times larger in magnitude than the loss modulus, indicating that more energy is being stored, rather than dissipated, in these materials. The storage stiffness increases with increasing strain (Fig. 8c) and is corroborated by quasi-static compression tests utilizing a simultaneous continuous stiffness measurement (CSM) (Fig. 8b), which is capable of better identifying the elastic regime and successive stiffness drops, while the initial peaks are smoothed over in storage stiffness data. The transition between plateau and densification is clearly visible in both, but is less pronounced in loss stiffness (factor of 3) compared with storage stiffness (factor of 5). Unlike the storage stiffness, the loss stiffness is a strong function of frequency and is generally lower at higher frequencies, though it appears to be slightly bowl-shaped. Unfortunately the cut-off frequency for our instrument prevents study of higher frequencies to verify this at higher frequencies. This frequency dependence is a reasonable observation since loss mechanisms are deformation-rate dependent. Thus, over the range of frequencies studied, the energy dissipation mechanisms appear to require a timescale longer than is afforded by a 35 Hz oscillation, with this trend being most evident at larger strains. Because attaining larger strains implies that a higher fraction of the pillar has buckled, we surmise that more energy is dissipated in the buckled portion of the pillar than in the remaining undeformed portion, and this dissipative process corresponds to a time constant of ~0.1 s. Simultaneously, the storage modulus indicates that even more energy is being stored in the buckled region.

3. Conclusions

We report that the uniaxial deformation of CNT bundles is accommodated by sequential nucleation of local buckles followed by their lateral propagation across the bundle, gradually collapsing a horizontal slice of the entire structure in a periodic fashion. Buckles occur successively, from bottom to top, due to the density and accompanying stiffness gradient of the as grown material. Stress–strain behavior is foam-like, but the stress does not remain constant in the plateau regime, and oscillations correspond to buckling nucleation and propagation rather than to individual cell collapse. Stress-rate dependence is marked by the oscillations’ shape: sinusoidal for slower rates, sharper sine-squared like shape for faster rates. Frequency dependence of loss modulus indicates timescale sensitive energy dissipation mechanism, largely contained within the buckled region of deformed pillars. Efforts are currently underway to develop phenomenological and viscoelastic models describing this unique deformation behavior.

4. Experimental

CNT Pillar Growth: We grew CNT bundles on a generic Si wafer (with ~300–400 nm thermal oxide) patterned using “contact” photolithography, then cleaned with O2 plasma. We evaporated ~3.0–3.5 nm of Al and vented the chamber to atmosphere to allow the Al to oxidize, forming an Al2O3 barrier layer. Next, a ~2.5–3.0-nm layer of active catalyst Fe was evaporated. The lift-off process removed the photoresist, leaving only the patterned catalyst, and the wafer was placed in a 2-in.-diameter quartz tube in a single-zone furnace outfitted with a vacuum exhaust and automated throttle valve. We first purged and filled with Ar (99.9999% pure Ar, UHP grade from Airgas) 3 times, then controlled pressure at 200 Torr while flowing Ar at 500 sccm and ramping the temperature to 675 °C. When the temperature was stable at 675 °C, we quickly switched out Ar and started to flow 500 sccm of ethylene (99.99% C2H4, Research Grade from Airgas) to grow the multiwalled CNTs. Run times were typically between 15 and 30 min. To end growth, the Ar and ethylene were quickly switched again and the furnace was allowed to cool to near room temperature under flowing Ar.

Mechanical Testing: Samples were chosen from the array of grown pillars by using an SEM according to two criteria: the pillar is perpendicular to the substrate and the aspect ratio is between 1 and 1.5. Mechanical experiments utilized the XP module of Agilent’s nanoindenter G200 with custom TestWorks software control methods written by the authors. The pillars were compressed by a diamond flat punch of ~95-μm diameter, custom-milled by the authors from a Berkovich tip by using a focused ion beam (Nova 200, FEI Company) in conjunction with a selective carbon mill. Prior to acquiring data, we characterized the nanoindenter by using the methods outlined in Herbert et al. [14] to locate the cut-off frequency.

Load–displacement data were gathered at a constant prescribed displacement rate by using proportional control of the inherently load-controlled instrument. This resulted in maximum percent errors of (2 × 10−3)% for the slowest rate and 0.25% (up to 0.4% for beginning of
unload) for the fastest rate. The top surface of the pillar was detected by setting the initial approach speed to $\sim$50 nm s$^{-1}$ while oscillating the indenter head at a fixed harmonic load (resulting in $\sim$30-nm amplitude) at 25 Hz and waiting for the harmonic stiffness to exceed 50 N m$^{-1}$. The oscillation was then turned off, and the test began by loading at the prescribed strain rate to a prescribed depth. At the peak load, a short hold (on the order of three time constants of the capacitive displacement gauge, $\sim0.003$ ms) allowed the displacement gauge to recover from any offset between the real-time and reported position, if necessary. The pillar was then unloaded at the same prescribed displacement rate until the displacement became less than the displacement at the surface. Surface contact was lost before this point is reached. After compressing the pillar, the test runs a series of holds in air starting at the raw displacement of the pillar surface and going to the full compression depth in order to correctly account for the machine’s contribution to the raw load and displacement measured as discussed in Section 2.2.1.

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