

# 1 Strain-Engineered Manufacturing of Freeform Carbon Nanotube 2 Microstructures

3 *M. De Volder*<sup>1,2,\*†</sup>, *S. Park*<sup>3,4,\*</sup>, *S. Tawfik*<sup>3,4,5</sup>, *A.J. Hart*<sup>3,4,†</sup>

4 <sup>1</sup>*Institute for Manufacturing, University of Cambridge, 17 Charles Babbage Rd, Cambridge, CB3*  
5 *0FS, UK*

6 <sup>2</sup>*IMEC, Kapeldreef 75, 3001 Heverlee, Belgium, Department of Mechanical Engineering, Katholieke*  
7 *Universiteit Leuven, 3001 Leuven, Belgium*

8 <sup>3</sup>*Mechanosynthesis Group, Department of Mechanical Engineering, University of Michigan, 2350*  
9 *Hayward Street, Ann Arbor, Michigan 48109 USA*

10 <sup>4</sup>*Mechanosynthesis Group, Department of Mechanical Engineering, Massachusetts Institute of*  
11 *Technology, 77 Massachusetts Ave, Cambridge, Massachusetts, 02139 USA*

12 <sup>5</sup>*Mechanical Science and Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois,*  
13 *61822 USA*

14 *\*These authors contributed equally.*

15 <sup>†</sup>*Corresponding authors: M. De Volder: [mfld2@cam.ac.uk](mailto:mfld2@cam.ac.uk), A.J. Hart: [ajhart@mit.edu](mailto:ajhart@mit.edu)*

16

## 17 Abstract

18 The skins of many plants and animals have intricate micro-scale surface features that give rise to  
19 properties such as directed water repellency and adhesion, resistance to fouling, and camouflaging.  
20 However, engineered mimicry of these designs has been limited by the capabilities of creating  
21 complex forms by top-down fabrication processes. We demonstrate a new technique for scalable  
22 manufacturing of freeform microstructures, via strain-engineered growth of aligned carbon nanotubes  
23 (CNTs). Lithographic patterning of the CNT growth catalyst is used to locally modulate the CNT  
24 growth rate, which causes collective bending during growth with exceptional uniformity. The final  
25 shape of the curved CNT microstructures can be approximated via finite element modeling, and  
26 compound catalyst shapes produce microstructures with multi-directional curvature and unusual self-  
27 organized patterns. Conformal coating of the CNTs enables tuning of the mechanical properties  
28 independently from the microstructure geometry, representing a versatile principle for design and  
29 manufacturing of complex microstructured surfaces.

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## 34 **Introduction**

35 Scalable fabrication of microstructures that mimic the hierarchical surface designs found in nature  
36 has been a long-standing aspiration of material scientists [1-5]. While symbiotic growth of the  
37 integrated circuit (IC) and micro electro mechanical systems (MEMS) industries has enabled  
38 innovations in 3D fabrication that leverage semiconductor processing tools, these methods, such as  
39 interference or inclined exposure lithography are typically limited to arrays of identical structures [6-  
40 8]. Rapid prototyping methods such as direct laser writing, multiphoton lithography, and focused ion  
41 beam milling can create arbitrary forms but are serial, and therefore have lower areal throughput [9,  
42 10]. It is also especially difficult to fabricate surface structures having curved and/or re-entrant  
43 geometries.

44 On the other hand, use of locally directed actions, such as mechanical stresses, capillary forces,  
45 and electromagnetic fields, along with their interactions with templates, offers opportunity to create  
46 novel self-organized geometries and to design fabrication processes that achieve attractive  
47 combinations of dimensional control and throughput [2, 8, 11-15]. Examples abound in soft materials  
48 and chemical systems including micro-scale reaction-diffusion patterns [16, 17], self-assembly of  
49 block copolymers [18], and helical aggregation of polymer nanopillars [19, 20]. However, many of  
50 these processes need further development to achieve structural uniformity over large substrates.

51 We present a novel approach taking advantage of microscale top-down lithographic patterning in  
52 conjunction with nanoscale self-organization, which enables large-area fabrication of freeform  
53 microstructures made of aligned carbon nanotubes (CNTs). This process leverages the influence of  
54 the catalyst-substrate interactions on the growth rate of CNTs [21], creating stress gradients during  
55 synthesis that guide the CNTs into curved microscale geometries. Our method is analogous to the  
56 well-known use of thin film stress to create curved and folded MEMS structures [22]. However,  
57 because our process is based on an additive chemical synthesis process instead of a subtractive etching  
58 and release technique, it enables the direct synthesis of complex microstructures that are perpendicular  
59 rather than parallel to the substrate. This has two major implications: it enables fabrication of closely  
60 packed arrays of structures with heterogeneous shapes, and the porosity of the CNT forests enables  
61 conformal coating after growth to modify chemical and/or mechanical properties. We demonstrate  
62 this latter point by conformal coating of CNT “microtruss” arrays by atomic layer deposition (ALD)  
63 and polymer CVD, which increases their mechanical stiffness without changing the geometry.

## 64 **Results**

65 **Fabrication.** CNTs grown by chemical vapour deposition (CVD) from a high-density  
66 arrangement of catalyst nanoparticles on a substrate are known to self-organize into vertically aligned  
67 assemblies often called “CNT forests” [23, 24]. We first observed that the density and rate of CNT  
68 forest growth from a widely studied supported catalyst (Fe/Al<sub>2</sub>O<sub>3</sub>, 1/10 nm) can be influenced by the  
69 material immediately beneath the catalyst. This premise is shown in **Fig. 1a**; patterning of CNT  
70 growth catalyst (Fe/Al<sub>2</sub>O<sub>3</sub>) on a SiO<sub>2</sub>/TiN “checkerboard” followed by exposure to standard CVD  
71 conditions (see Methods) results in a “bi-level” CNT micropillar array. The catalyst patterns directly  
72 on SiO<sub>2</sub> grow CNTs to ~100 μm (in < 2 minutes), whereas the patterns on TiN (upon SiO<sub>2</sub>) grow  
73 CNTs to 50 μm in the same time span. In **Fig. 1b**, “tri-level” CNT forests are grown by arranging  
74 patches of catalyst on SiO<sub>2</sub>, 70 nm TiN, and 140 nm TiN. This principle could be extended to an  
75 arbitrary number of levels or even continuous height gradients via additional lithography and  
76 underlayer deposition steps that modulate the growth rate via catalyst-substrate interactions.

77 Next, we used the above differential growth principle to design compound catalyst/underlayer  
78 patterns that directly form curved CNT forest geometries. If a continuous micro-scale catalyst pattern  
79 is placed partially on SiO<sub>2</sub> and partially on TiN, the differential growth rates induce stress within the  
80 CNT microstructure. For example, as shown in **Fig. 2a and 2b**, a square catalyst pattern with half of  
81 its area on the TiN layer bends toward the side which is upon TiN, due to the difference in growth rate  
82 on the coupled halves of the structure. The stress is transferred between contacting CNTs at the  
83 boundary region via mechanical entanglement and van der Waals interactions among the CNTs.  
84 Depending on the curvature and length of the structures, slanted micropillars (**Fig. 2a**), or arches (**Fig.**  
85 **2b**) can be fabricated. Because the local interaction and differential growth rate determines the  
86 trajectory of each structure, large arrays with nearly identical anisotropic shapes can be produced as  
87 shown in the SEM images. Importantly, these 3D structures are fabricated using only two standard  
88 photolithography steps, one for patterning the TiN layer, and one for patterning the catalyst layer.

89 The curvature can be controlled by designing the amount of overlap between the catalyst and the  
90 TiN underlayer. This is illustrated in **Fig. 3a and b**, which respectively show arrays of round and  
91 square cross-section micropillars where the overlap distance is varied from left to right (increments of  
92 5 μm). As expected, the portion of the pillars growing on TiN is always shorter, and as a result, all  
93 pillars bend towards the TiN side. As the portion of overlap decreases, the stress induced by the  
94 differential growth rate causes increased bending (smaller radius of curvature), reaching a maximum  
95 when the catalyst shape is split symmetrically by the TiN layer. With <50% overlap on TiN, the  
96 curvature increases gradually until the structure is only slightly curved at the rightmost extent of the  
97 array. The CNTs are generally tangential to the curvature of the microstructures, similar to the CNT  
98 alignment observed in CNT forests.

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100 **Static model of stress-driven CNT curvature.** The coupling of stress and CNT growth rate, via  
 101 the anisotropic mechanics of the CNT forest [25], is a complex problem. However, we find that a  
 102 static mechanical model analogous to that used for differential expansion of a bi-material cantilever  
 103 beam can reasonably predict the curvature of CNT structures grown from an overlapped catalyst/TiN  
 104 rectangle. Starting from the classical formulation of the bimetallic strip model [26], we replace the  
 105 temperature-dependent expansion term by a differential lengthening term representing the CNT  
 106 growth rate. Accordingly, the curvature of the compound CNT microstructure is described as:

$$107 \frac{1}{\rho} = \frac{6\left(\frac{R_1 - R_2}{R_1}\right)(1+m)^2}{w\left(3(1+m)^2 + (1+mn)\left(m^2 + \frac{1}{mn}\right)\right)} \quad (1)$$

108 Here  $\rho$  is the radius of curvature,  $R_1$  and  $R_2$  are the growth rates (1 denotes CNTs on Fe/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>  
 109 and 2 denotes CNTs on Fe//Al<sub>2</sub>O<sub>3</sub>/TiN), and  $w$  is the CNT micropillar width. In addition,  $m$  and  $n$  are  
 110 defined as

$$111 m = \frac{w_2}{w_1}, n = \frac{E_2}{E_1} \quad (2)$$

112 where  $w$  denotes the width and  $E$  denotes the respective Young's Moduli of the segments. The value  
 113 of  $n$  is specified as 0.6 which is the ratio of the measured areal mass density of CNTs on the respective  
 114 underlayers; however, because the elongation of each layer is specified in the model, the output is  
 115 insensitive to this value. The geometric parameters are defined in **Fig. 3c**.

116 Using the calculated curvatures, and the weighted average growth rate, the shapes of the resultant  
 117 CNT microstructures were visualized using Matlab. The simulation results correspond to the rows of  
 118 structures in the SEM image **Fig. 3b**. To compare the experiments to the simulation, the tip position  
 119 was characterized in horizontal and vertical axes, normalized to the base dimension ( $w$ ), as shown in  
 120 **Fig. 3c**. For both the experiment and simulation, the x position of the tip reaches its maximum at 0.4  
 121 overlap, and the y position reaches its minimum at approximately 0.6-0.7 overlap.

122 The differences between the predicted and calculated displacements arise because the model does  
 123 not capture the exact kinetics of CNT growth, which varies with time. Moreover, it cannot consider  
 124 how the stress between the two portions of the structure, which are idealized as perfectly coupled  
 125 without slip, influences the deformation. CNT forests have anisotropic mechanical properties, with  
 126 the lateral stiffness (perpendicular to the CNT alignment) typically much less than the axial stiffness  
 127 [27], therefore in principle favoring greater deflection due to built-in stress gradient. Local wrinkling  
 128 and buckling of the CNTs in the compound microstructures indicates that the growth stress causes  
 129 complex mechanical deformations, which cannot be predicted by linear elasticity and the bimaterial  
 130 deflection model (see Fig. 4a).

131 To gain further insight into the mechanical coupling causing stress-driven bending, we designed a  
 132 “striped” structure where alternate catalyst/underlayer regions are coupled with a large interfacial area.  
 133 This structure is symmetric, so it grows straight vertically yet has significant internal stresses. As  
 134 shown in Fig. 4a and the neighboring insets, the faster growing CNTs deform collectively into a

135 wavelike pattern. Therefore, while the vertical growth rate of the structure is matched at the interface,  
136 the faster growing side still accumulates longer CNTs and these CNTs bend and possibly buckle to  
137 accommodate their additional length. This deformation mode is similar to what is observed in  
138 mechanically compressed forests [28].

139 As seen in **Fig. 3a** and supplementary figure **1a**, some structures separate at the interface between  
140 the differentially growing regions, due to shear stresses at the interface. In future work, this could be  
141 remedied by adapting the structure design to reduce the interfacial shear stress between the segments,  
142 or by using a more gradual growth rate gradient to accommodate the stress gradient, such as a three-  
143 layer design as in **Fig. 1b**. However, we importantly find that structures that do not separate during  
144 synthesis can withstand large subsequent deformations without failure. For instance, supplementary  
145 figure **1b** shows an SEM image of an arrangement of bent pillars during compression to 50% vertical  
146 strain, at which point delamination at the interface begins only where the pillars kink near their  
147 midsection.

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#### 150 **CNT and catalyst morphology.**

151 The strain-engineered CNT microstructures show differing CNT density and alignment in the fast  
152 and slow growing portions. In **Fig. 4a,b**, the CNTs grown from catalyst on TiN appear to have greater  
153 vertical alignment influenced by the interface with the faster-growing region. On the other hand, the  
154 CNTs grown from catalyst on SiO<sub>2</sub> are less aligned, due to the retarding force from the slower-  
155 growing mating regions.

156 We hypothesized that the differential CNT growth behavior on the TiN underlayer may be  
157 attributed to differences in the catalyst morphology, which can influence the CNT diameter  
158 distribution and number density. Atomic Force Microscopy (AFM) showed that as-deposited catalyst  
159 layers on SiO<sub>2</sub> and TiN have a similar topology (supplementary figure **2**). However, upon annealing in  
160 H<sub>2</sub>/He prior to hydrocarbon exposure (see methods), the TiN-catalyst layer forms shallow mounds,  
161 tens of nanometers high and hundreds of nanometers wide, in addition to smaller catalyst particles.  
162 The control case of catalyst on SiO<sub>2</sub> does not exhibit such topography. For samples with 80 nm TiN  
163 layer, the average catalyst particle height and spacing were calculated to be 5.2 nm and 19 nm  
164 respectively. Compared to those on SiO<sub>2</sub> (7.5 nm and 18 nm, respectively [29]), the catalyst particle  
165 sizes are smaller on average while the spacing is comparable. In addition, the Root Mean Square  
166 (RMS) roughness of the annealed catalyst/TiN layer is 5.6 nm, which is considerably higher than that  
167 of catalyst on SiO<sub>2</sub> (1.4 nm).

168 Small Angle X-ray Scattering (SAXS) was used to further investigate the CNT forest morphology  
169 [30, 31]. For this experiment, CNTs were grown for 10 minutes on SiO<sub>2</sub>, and on 40 nm, and 80 nm  
170 TiN layers; these samples reached lengths of 800, 500, and 400  $\mu\text{m}$  respectively. The scattered X-ray  
171 intensities were fitted to a mathematical form factor model for hollow cylinders [32] to calculate the

172 diameter and Herman's orientation parameter, which is a measure of alignment. Both the CNT  
173 diameter (**Fig. 4e**) and alignment (supplementary figure 3) are shown to be lesser for increasing TiN  
174 underlayer thickness. Specifically, CNTs on SiO<sub>2</sub> have initial average diameter of 9.5 nm, while CNTs  
175 on TiN are approximately 8 nm in diameter. These measurements further support the AFM data which  
176 showed that the catalyst particles on TiN layers are smaller than those on SiO<sub>2</sub>. The decrease in  
177 diameter with growth time has been attributed to diffusion of the catalyst into the Al<sub>2</sub>O<sub>3</sub> [30, 33]. The  
178 Herman's orientation parameter increases from the top of the forest (the initial growth), then reaches a  
179 maximum, and then decreases toward the bottom of the forest. This trend is typically observed for  
180 CNT forests grown by CVD, and has been attributed to density variation due to collective activation  
181 and deactivation of the growing CNT population [30]. The measured areal mass density of the CNT  
182 forests is 0.011 mg mm<sup>-2</sup> on 80 nm TiN and 0.018 mg mm<sup>-2</sup> on SiO<sub>2</sub>. Therefore, these methods  
183 consistency show that placement of the TiN layer under the catalyst results in CNT forests with a  
184 smaller average CNT diameter, lesser alignment of CNTs, and a lower density. Although we have not  
185 directly compared the mechanical properties of the different segments, we expect that the CNT forests  
186 on TiN have lower stiffness, and lesser anisotropy in mechanical properties. The positive correlation  
187 between CNT density and alignment is also expected based on recent literature, which demonstrated  
188 that CNT-CNT crowding controls alignment within non-patterned forests [34].

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190

## 191 **Discussion**

192

### 193 **Complex 3D microstructures**

194 Based on our understanding of the elementary catalyst/underlayer designs that achieve  
195 unidirectional bending, we designed a variety of more complex patterns that produce exemplary CNT  
196 microstructures having complex curvature. For instance, a compound shape consisting of a "+"  
197 catalyst microfeature with each arm offset by a rectangular TiN underlayer results in growth of twisted  
198 CNT microstructures (**Fig. 5a**), resembling macroscale propellers. The first-order applicability of the  
199 bimaterial bending model discussed above inspired us to evaluate the suitability of finite element  
200 modeling (FEM) to predict the shapes of these structures. These were simulated using Comsol FEM  
201 software as illustrated in **Fig. 5a**, capturing the uncoupled differential growth rate (**Fig. 1a**) as a 50%  
202 expansion mismatch, and estimating the Young's modulus as 30 MPa for the CNTs on TiN and 50  
203 MPa on SiO<sub>2</sub> [35].

204 Similarly, thin semicircles of CNTs can be directed to curve outward by offsetting the TiN  
205 underlayer as shown in **Fig. 5b**. Further structural complexity is shown by the scrolling of thin offset  
206 rectangular patterns (**Fig. 5c**). Last, exotic hierarchical arrangements can be formed by the interaction  
207 of closely spaced structures, such as the self-organization of offset circular micropillars into wavy

208 patterns (**Fig. 5d**) that are reminiscent of macroscale crochet stitching. We hypothesize that, after the  
209 individual structures bend unidirectionally and contact one another, their continued growth and steric  
210 hindrance causes the wavy pattern to form. More investigation is needed to understand the complex  
211 deformations of these structures, and their relationship to the mechanics of the CNT forest and the  
212 mechanical feedback on the growth process itself.

213 Notably, in spite of the complex geometries and local deformations, all of these structures can be  
214 produced with impressive consistency over large arrays. Arrays of several hundred structures were  
215 examined and shown to exhibit nearly identical forms, with defects most frequently arising from  
216 debris due to the lithography process rather than the CNT growth step. In this study, we explored  
217 structures with critical dimensions as small as 5  $\mu\text{m}$  (**Fig. 5**), and found that the uniformity of the  
218 structures was not sacrificed at this scale. We expect that smaller 3D microstructures could be made  
219 while still using optical lithography along with high-precision alignment of the catalyst and TiN  
220 layers. Notably, sub-micron vertical CNT features have been fabricated for use as interconnects [36].  
221 Further, because the curved and twisted geometries result from collective behavior of CNT forest  
222 growth, we expect the structures to require a certain minimal size to average out the stochastic  
223 variation of individual CNT growth rate and catalyst lifetime. Considering the approximate CNT-  
224 CNT spacing within the current microstructures ( $\sim 100$  nm), the minimal feature size of reliable growth  
225 of curved microstructures may be limited to  $\sim 1$   $\mu\text{m}$ , though this requires further investigation.

226

### 227 **Post-processing and mechanical reinforcement**

228 Last, we show that 3D CNT structures can be post-processed via both wet and dry methods that  
229 enable tuning of their properties and functionality. Low-density bent CNT micropillars can be  
230 transformed into robust densely packed CNT structures by capillary forming (**Fig. 6a-b**) [35, 37, 38].  
231 To do so, the substrate is exposed to a stream of heated acetone vapor, causing acetone to condense  
232 onto the CNTs and substrate, and infiltrate each CNT microstructure. Upon subsequent evaporation of  
233 the acetone, the CNT forest shrinks laterally, due to the surface tension of the shrinking meniscus.  
234 Previously, we showed that capillary forming of vertical CNT microstructures increases the Young's  
235 modulus in compression approximately 100-fold, from  $\sim 50$  MPa to 4 GPa [35]. These values are  
236 comparable to soft rubbers and stiff epoxies, respectively. Moreover in the present case the capillary  
237 forming process preserves the curved geometry and increases the lateral deflection.

238 Alternatively, curved CNT microstructures can be coated conformally via vapor phase methods,  
239 thereby enabling decoupled control of geometry and mechanical properties. To investigate this, we  
240 fabricated CNT "microtruss arrays" (**Fig. 6c-e**), which are analogous to truss designs used in  
241 composite materials to achieve high strength and energy absorption at relatively low density [40-42].  
242 The CNT microtrusses each consist of four corner members and a central pillar, meeting at an apex.  
243 We explored coating of the CNT microtrusses with both parylene (by chemical vapor deposition,  
244 CVD, supplementary figure 4) and alumina (by atomic layer deposition, ALD, **Fig. 6d**). Upon vapor

245 phase infiltration of the precursors, the CNTs and bundles within the forest are coated individually and  
246 conformally [43], enabling fine-tuning of their porosity and mechanics without altering the  
247 microstructure geometry. Via flat punch compression testing, we found that a 51 nm Al<sub>2</sub>O<sub>3</sub> coating on  
248 the CNTs increases the mechanical stiffness by more than 100-fold; typical loading-unloading curves  
249 are shown in **Fig. 6e** and supplementary figure 4 for different coating materials and thicknesses. The  
250 equivalent stiffness range of the 3D CNT microtrusses is 0.36 to 54 kN m<sup>-1</sup>, which spans typical values  
251 of MEMS springs used in probe card arrays [44]. A further attribute of the TiN underlayer is its  
252 electrical conductivity. In the future, electrical integration of strain-engineered CNT structures in  
253 conjunction with the post-processing methods described above could be useful in advanced  
254 microsystems, including as structural elements or microsensors [45, 46]. Such applications could take  
255 advantage of the thermal and mechanical durability of CNTs, as well as the anisotropic properties  
256 arising from their alignment and collective curvature.

257 The ability to fabricate large arrays of 3D microstructures is also conducive to mimicry of nature's  
258 advanced functional materials [5]. We say this because the structures shown in Fig. 2 and 5 have  
259 similar size and geometry to butterfly wings that have anisotropic wetting properties [47], dry  
260 adhesive contacts on the legs of beetles and gecko lizards [3], and microscale sensing hairs found on  
261 spiders [39]. Therefore, we suggest that 3D CNT microstructures offer opportunities to further  
262 engineer the excellent dry adhesive [48, 53] and superhydrophobic [54] properties previously reported  
263 for CNT forests. For mechanical applications such as dry adhesion, an important consideration is the  
264 adhesion of the structures to the substrate, as well as the mechanical resilience of the structures upon  
265 repeated loading. While we have found that the segments of the curved structures are well adhered to  
266 each other (supplementary figure **S1b**), we anticipate that coating or transfer steps may be necessary  
267 to anchor the structures for use as robust surface contacts [48]. Exploration of potential optical and  
268 photonic applications would require further miniaturization of the structures. Nevertheless, combined  
269 with the emerging methods to grow and pattern CNT forests on large-area substrates [49-51], we are  
270 optimistic that the methods shown here can enable large-area surface coatings having advanced  
271 functionalities.

272  
273 In summary, we show that strain-engineered CNT growth enables the scalable fabrication of  
274 complex 3D microstructures having unidirectional and multidirectional curvature. The capability to  
275 produce such structures *en masse* using only 2D patterning methods along with standard thermal  
276 processing contrasts the limitations of many existing processes that require serial processing or  
277 sequential exposure using complex inclined lithography methods. Moreover, the structures can profit  
278 from the mechanical robustness and electrical conductivity of CNTs, and their mechanical and surface  
279 properties can be engineered independently from their geometry by conformal coating of the CNTs  
280 after growth. This represents a highly attractive principle for materials design, and is promising for  
281 | scalable manufacturing of 3D microstructured surfaces having biomimetic properties.

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294 analysis.

295

296 **Author Contributions**

297 M.D.V., S.H.T. and A.J.H. conceived the research topic. All authors designed the experiments.  
298 M.D.V., S.J.P., and S.H.T. fabricated and characterized the materials. S.J.P. performed simulations.  
299 All authors discussed the results, wrote and reviewed the manuscript.

300

301 **Methods**

302 Substrate patterning and CNT growth

303 The catalyst and TiN layers are patterned on (100) silicon wafers with 300 nm of thermally grown  
304 SiO<sub>2</sub>. Each layer is patterned by lift-off processing, by photolithography (photoresist IX845) followed  
305 by ultrasonic agitation in acetone. The TiN layer is deposited and patterned first, and then the catalyst  
306 layer (1 nm Fe upon 10 nm Al<sub>2</sub>O<sub>3</sub>) is deposited and patterned. The wafer is then diced into ~1×1 cm  
307 pieces, and the substrates are placed in the quartz tube furnace, and the CNT growth is performed. The  
308 recipe starts by with flowing 100/400 sccm of He/H<sub>2</sub> while heating to 775 °C over 10 minutes  
309 (ramping step); then the system is held at 775 °C for 10 minutes (annealing step) while maintaining  
310 the gas flow. Then 100 sccm of C<sub>2</sub>H<sub>4</sub> is added to the gas mixture at 775 °C for CNT growth for the  
311 desired duration. The typical growth rate is ~50 μm/minute on Fe/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>. Once the CNTs have  
312 grown, C<sub>2</sub>H<sub>4</sub> is removed from the gas mixture and the furnace is cooled to <100 °C. After cooling, the  
313 system is purged with He before the sample is removed. Optionally, C<sub>2</sub>H<sub>4</sub> flow can be maintained  
314 while cooling down to improve the adhesion of the CNT microstructures to the substrate. Once the  
315 cooling step is complete, the quartz tube is purged with 1000 sccm of He for 5 minutes before opening  
316 up the end caps and retrieving the samples.

317 Small Angle X-ray Scattering (SAXS):

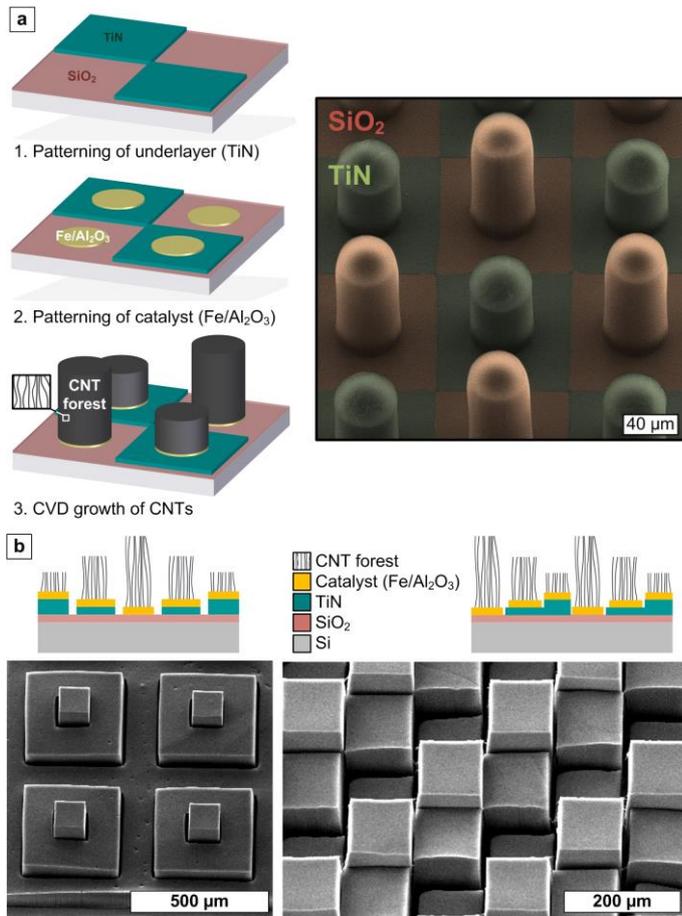
318 SAXS characterization of CNT microstructures was performed at the Cornell High Energy  
319 Synchrotron Source (CHESS) using the G1 beamline (10±0.1 keV, 0.13nm wavelength). The beam is  
320 focused to a 10μm spot using a single bounce monochromator. The CNT sample is placed on a  
321 motorized stage and the focused X-ray beam is passed through the sample. The scattered beam is  
322 collected using a 2D detector and the measured intensities were normalized to the original intensity  
323 measured by another detector at upstream of the CNT sample. The scattering data is then fitted to a  
324 mathematical model assuming a log-normal distribution of hollow cylinders to calculate the CNT  
325 diameters as well as the Herman's parameter for CNT alignment. The detailed procedure is described  
326 by Bedewy et al. [30].

327

328

329 **Figure Captions**

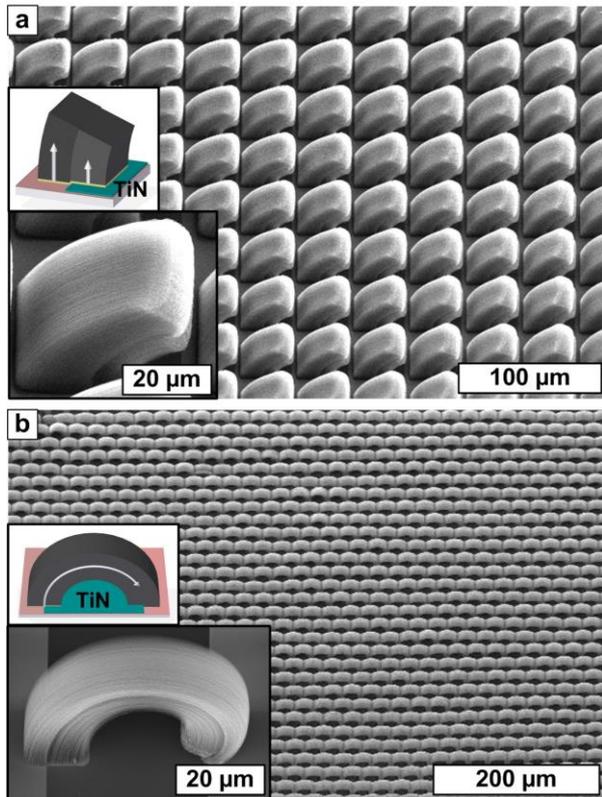
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331

332 **Figure 1.** Multi-height CNT micropillar growth using TiN as a rate-controlling catalyst underlayer. (a)  
333 Process steps including two lithography steps, and accompanying (color added) pattern of cylindrical  
334 CNT micropillars grown on “checkerboard” of alternating TiN (80nm thickness) squares on SiO<sub>2</sub>. (b)  
335 Triple-height arrays made by substrate and catalyst patterning with three lithography (TiN layers are  
336 40 nm and 80 nm thickness).

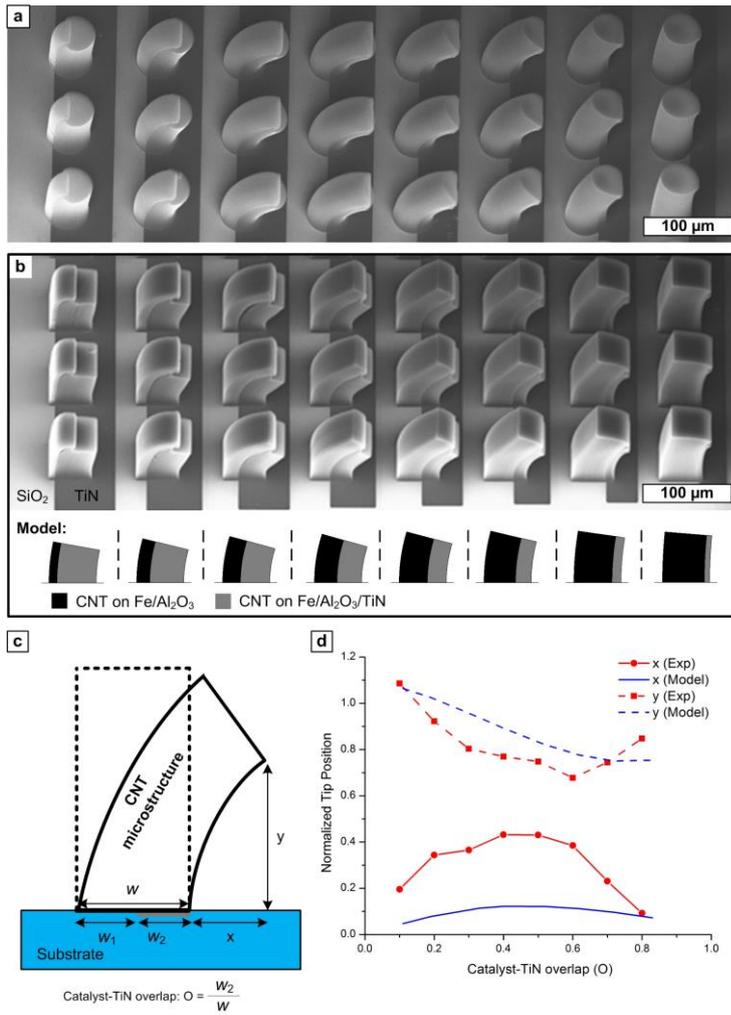
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338

339 **Figure 2.** Curved CNT micropillars grown from catalyst rectangles partially overlapping TiN. The  
 340 pillars bend toward the TiN side, which grows more slowly and couples to the faster-growing region  
 341 of catalyst directly on SiO<sub>2</sub>. (a) Closely-spaced short structures with ~45° takeoff angle. (b) Arch-like  
 342 structures that curve over and contact the substrate at their distal ends.

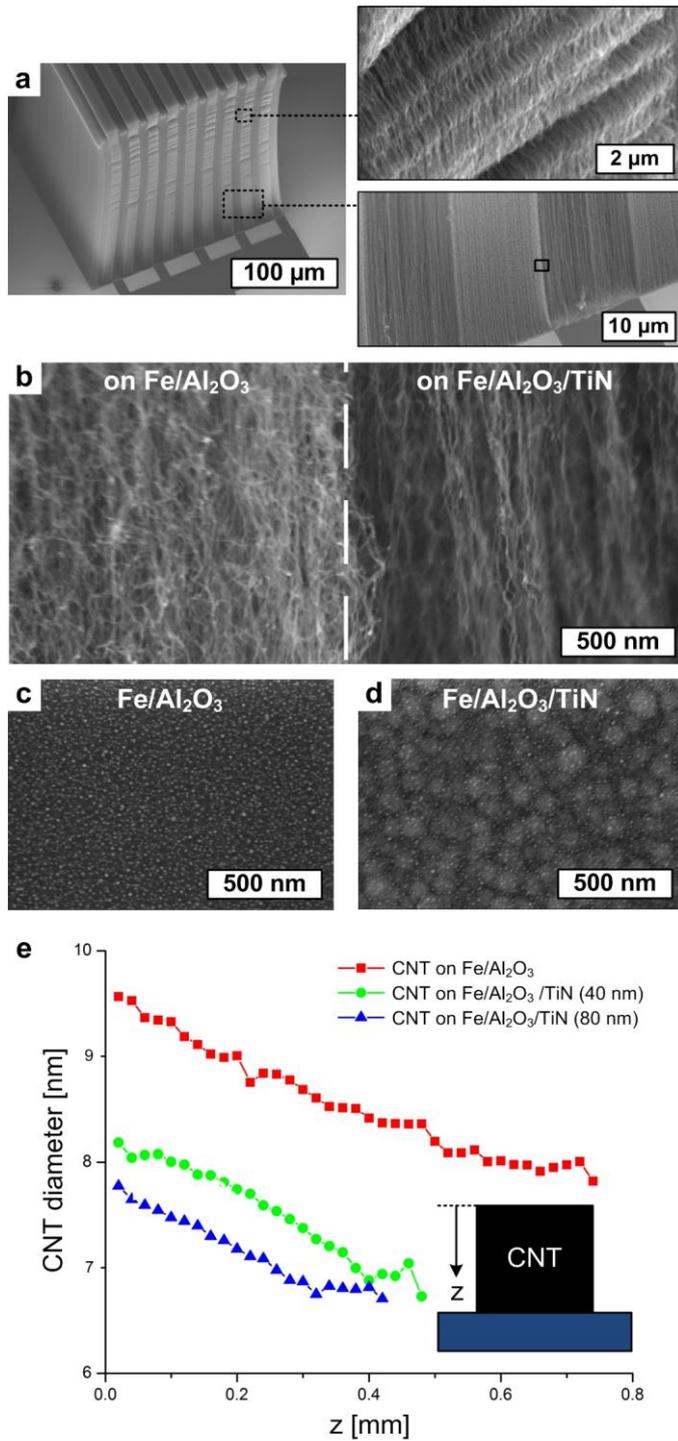
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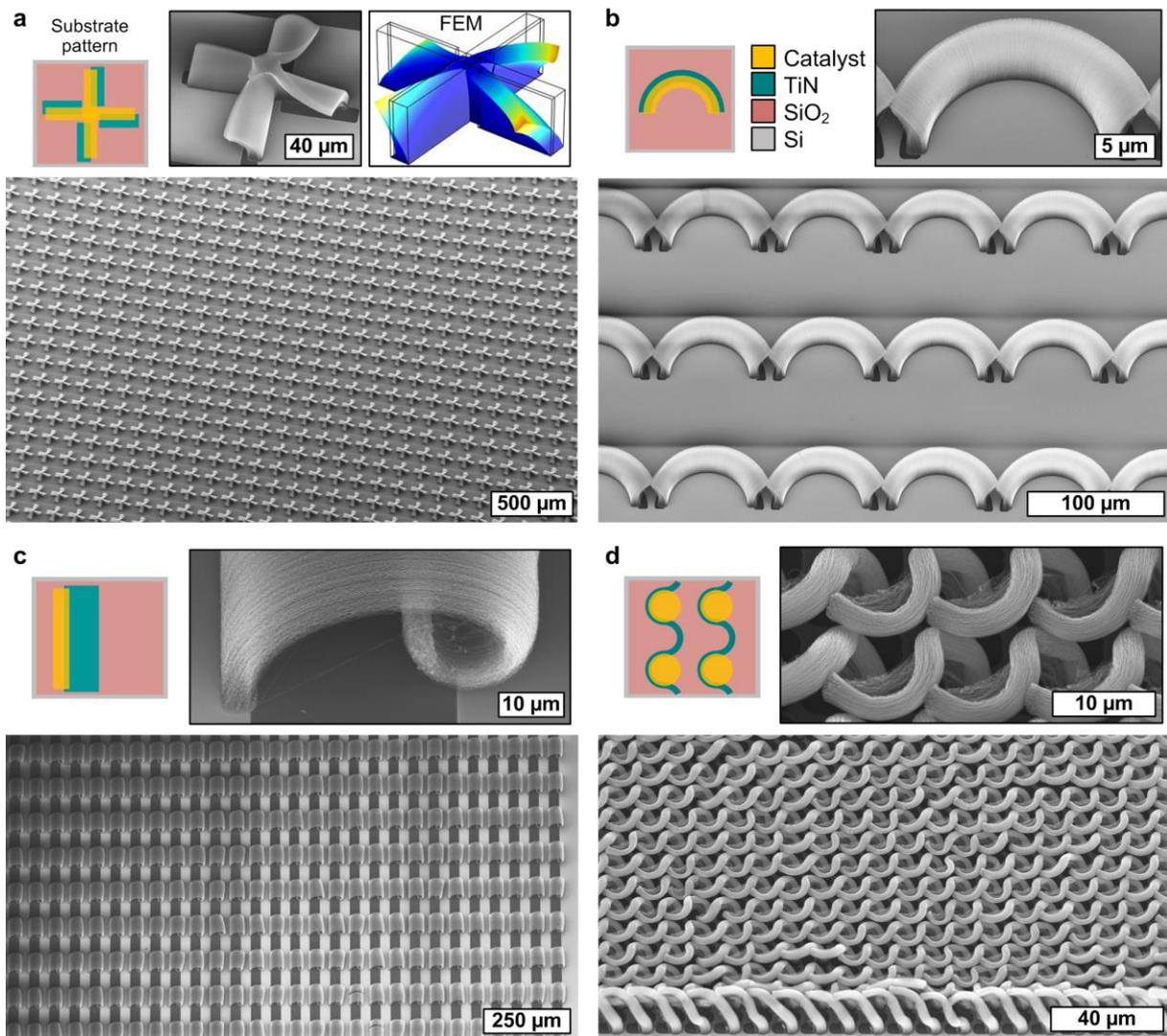
345 **Figure 3.** Shape gradients and their use in elementary modeling of the stress-driven CNT growth  
 346 process. (a,b) arrays of round and square CNT micropillars with decreasing catalyst/TiN overlap from  
 347 left to right. (c) Schematic of geometric parameters used to quantify deformation of square  
 348 micropillars. (d) Output of differential expansion model predicting vertical and lateral deflection  
 349 versus substrate pattern design, comparing simulations, inset to (b), and measurements from SEM  
 350 images.

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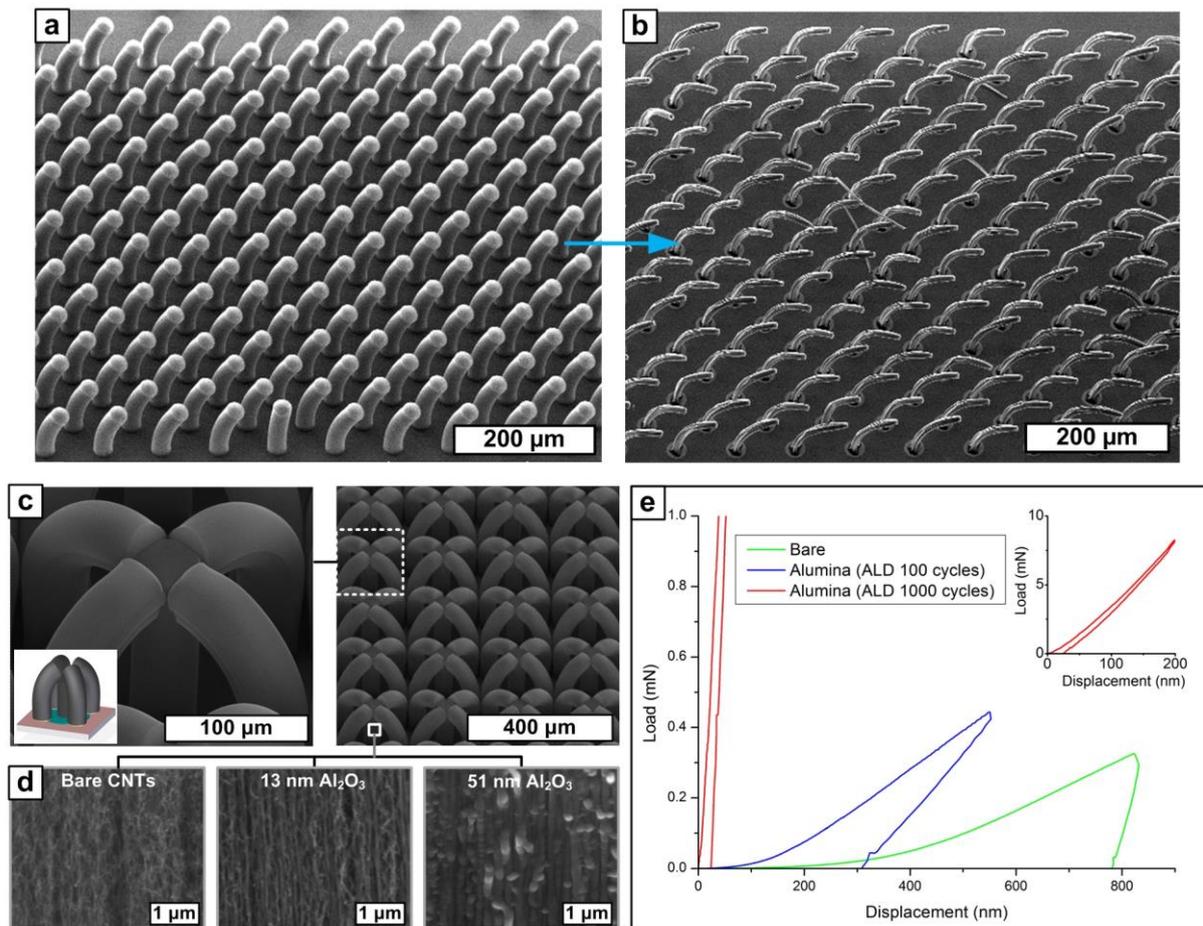
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353 **Figure 4.** Analysis of CNT morphology. (a) SEM image of micropillar with catalyst on fine stripes of  
 354 TiN, with close-up images showing the CNT morphology difference and evidence of internal stress  
 355 causing local deformation. (b) Close-up images of the aligned CNT morphology in adjacent segments  
 356 of the micropillar. (c,d) SEM images of the substrate morphology after annealing in H<sub>2</sub> and rapid  
 357 cooling, showing hierarchical morphology of nanoparticles on the catalyst/TiN area. (e) Diameter  
 358 mapping within the CNT forests, from fitting of SAXS data.



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360 **Figure 5.** Design and fabrication of arrays of complex microstructures. Each of the four panels  
 361 contains a sketch (top left) of the catalyst-TiN pattern used for CNT growth, a close-up SEM image  
 362 (top right), and an exemplary array of structures (bottom). (a) Twisted propeller-like structures,  
 363 made from azimuthally offset crosshair catalyst/TiN layers, also compared to finite element model  
 364 (FEM) prediction of shape (top right). (b) Outward curving semicircles made from radially offset  
 365 catalyst/TiN layers. (c) Scroll-like deformation of thin-walled microstructures with slight catalyst/TiN  
 366 overlap. (d) Collective organization of bending microstructures into a wavy pattern.



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369 **Figure 6.** Post-processing of 3DCNT microstructures. (a, b) Array of bending micropillars before and  
 370 after capillary forming, respectively. The unidirectional anisotropic morphology is maintained and the  
 371 micropillar cross section decreases, while the lateral deflection angle of the structures increases. (c)  
 372 Microtruss array fabricated to study mechanical reinforcement by vapor-phase coating of the CNTs.  
 373 (d) SEM images of aligned CNTs in the forest sidewall before and after coating with Al<sub>2</sub>O<sub>3</sub> by ALD.  
 374 (e) Load-displacement curves before and after ALD coating, where the stiffness is measured from the  
 375 slope of the unloading curve.

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