Structurally Programmed Capillary Folding of Carbon Nanotube Assemblies

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ABSTRACT:

We demonstrate the fabrication of horizontally aligned carbon nanotube (HA-CNT) networks by spatially programmable folding, which is induced by self-directed liquid infiltration of vertical CNTs. Folding is caused by a capillary buckling instability and is predicted by the elastocapillary buckling height, which scales with the wall thickness as \( t^{3/2} \). The folding direction is controlled by incorporating folding initiators at the ends of the CNT walls, and the initiators cause a tilt during densification which precedes buckling. By patterning these initiators and specifying the wall geometry, we control the dimensions of HA-CNT patches over 2 orders of magnitude and realize multilayered and multidirectional assemblies. Multidirectional HA-CNT patterns are building blocks for custom design of nanotextured surfaces and flexible circuits.

Manipulation of nanostructures in a locally specific yet parallel fashion requires control of surface interactions among nanostructures, and interactions between nanostructures and surrounding interfaces. Indeed, while aggregation and stiction of micro- and nanostructures due to capillary forces initially emerged as a nuisance for microfabrication technology,† the dominance of interfacial over bulk forces at small length scales is becoming an important tool to assemble and manipulate small structures in a local fashion.‡ For instance, the force exerted by the surface of a wetting liquid has been used to fold films of polymers,§ silicon, and silicon nitride and to fabricate miniature photovoltaic devices.¶ Surface forces of a melted solder droplet can act as hinges to fold polyhedra from planar micropatterns of copper and SU-8;¶ and lateral capillary forces during drying of colloidal solutions are widely exploited to assemble ordered monolayers of particles.

In particular, control of surface forces could overcome the challenges of assembly and integration of one-dimensional nanostructures (NFs), such as carbon nanotubes (CNTs) and semiconducting nanowires (SNWs). Notably, CNTs and SNWs have exhibited novel performance in transistors,§–¶ lasers,¶ and thermoelectrics, and they have been used as new tools for interfacing with cells and tissues. Integration of these nanostructures in device architectures requires precise control over the location, orientation and thickness of the individual device elements. This capability is inherently offered by lithographic patterning of thin films but not by current methods to grow and assemble nanofilaments. Methods include placing NFs on substrates via directed deposition of solutions guided by electric fields,† and directed liquid flows;¶ and mechanical planarization techniques such as rolling, shearing, and dipping into liquids, and that reorient vertically grown NFs to a horizontal configuration. Importantly, these methods have been limited to creating unidirectional assemblies. However, locally multidirectional and multilayered architectures, which are needed for design of next-generation circuits and interconnects, have only been achieved by multistep alignment and transfer printing methods.

Here we show that self-directed wetting of vertically aligned nanostructures enables folding of multidirectional
Fabrication of HA-CNT patches by structurally programmed capillary folding: (a) schematic of patterning, growth, and folding sequence; (b) SEM image of a thin wall of vertical CNTs before folding (left) and after folding (right); (c) corresponding high-resolution SEM images of CNT alignment before and after folding; and (d) large array of folding patterns having different dimensions.

Figure 1. Fabrication of HA-CNT patches by structurally programmed capillary folding: (a) schematic of patterning, growth, and folding sequence; (b) SEM image of a thin wall of vertical CNTs before folding (left) and after folding (right); (c) corresponding high-resolution SEM images of CNT alignment before and after folding; and (d) large array of folding patterns having different dimensions.

anisotropic networks by exploiting a capillary induced buckling instability. This new strategy arose from our observation of the patterned thin walls of vertically aligned CNTs (VA-CNTs) spontaneously fold when a solvent is condensed onto the substrate (Figure 1 and Supporting Information Video S1). The folding direction can be controlled by lithographically patterning self-directing features that resemble arrows at the edges of the catalyst line that determines the cross-sectional shape of the CNT wall. As a result, the folding transformation is structurally programmable via the geometric design of the catalyst pattern for CNT growth. This versatile and deterministic technique can directly create patches of horizontally aligned (HA-) nanostructures having any desired in-plane orientation. Thus, HA-CNT patches can be used as building blocks for complex multidirectional and multilayered nanostructure networks.

Figure 1 shows the result of capillary folding of VA-CNTs. A thin VA-CNT “wall” structure with arrows at its ends is grown by thermal chemical vapor deposition from a lithographically patterned catalyst film. This results in a “forest” of CNTs having a low bulk density (2 × 10¹⁰ CNTs/cm², 10 nm average outer diameter) yet high orthotropy (Figure 1c). Then, a solvent that wets the CNTs, such as acetone, is condensed onto the substrate, by holding the substrate above a beaker containing a small amount of the boiling liquid. Finally, the liquid is evaporated by letting the substrate dry under ambient conditions. After this process, it is observed that the wall has collapsed to the substrate, in the direction indicated by the arrows, resulting in a horizontally aligned CNT (HA-CNT) patch. Further, the packing density of the CNTs is approximately 10-fold greater in the HA-CNT patch, as measured by the ratio between the width of the VA-CNT wall and the thickness of the HA-CNT patch. (Figure 3)

The self-directed folding of patterned VA-CNT walls into HA-CNT patches is caused by a mechanical instability induced by capillary forces. The mechanism is understood by considering the collective deformations and motions of the CNTs, due to both internal and external capillary forces on the CNT forest. As the solvent is condensed on the sample, the high affinity of acetone to CNTs causes it to infiltrate the VA-CNT forest and to form a meniscus around its boundary as shown in Figure 2a. Within the forest, internal capillary forces draw the CNTs closer together by elastocapillary densification, as the capillary force exerted by the liquid in the spaces among the CNTs is balanced by the elasticity of the CNTs. Elastocapillary densification of CNTs throughout the forest results in a collective microscale deformation of the structure, as the CNTs move toward the centroid of the cross-section in order to minimize their overall elastic energy. The arrows determine the position of the centroid, which is slightly offset from the centerline of the wall; thus, during elastocapillary densification, the wall tilts in the direction of the arrows.

Moreover, the local in-plane curvature of the forest boundary (perimeter) determines the local curvature and height of the meniscus, resulting in a distribution of forces with varying heights and directions of action around the boundary of the wall. For the wall with arrows shown in Figures 1 and 2a, the meniscus rises higher at the concave wedge (right side) than the convex side (left). A solution to the Laplace equation for the meniscus height on both sides of the tilted wall indicates that the height of the meniscus changes as the forest tilts according to the equations

\[
h_{\text{in}} = \sqrt{2\kappa^{-1} \left(1 - \sin(\theta_c + \alpha - \pi/2)\right)}^{1/2}
\]

\[
h_{\text{out}} = \sqrt{2\kappa^{-1} \left(1 - \sin(\theta_c - \alpha + \pi/2)\right)}^{1/2}
\]

\[
\kappa^{-1} = \sqrt{\gamma / \rho g}
\]
Here, \( h_{\text{in}} \) and \( h_{\text{out}} \) are the meniscus heights as shown in Figure 4a, \( \theta_c \) is the contact angle between the CNT wall and the liquid, \( \alpha \) is the angle between the wall and the horizontal plane, \( k^{-1} \) is the capillary length, \( \gamma \) is the liquid surface tension, \( \rho \) is the liquid density, and \( g \) is acceleration of gravity. Based on these equations, the meniscus tends to be higher on the right side of the wall (the side facing the direction of tilt), as shown in Figure 2a. Thus, the equations indicate that the initial tilt of the wall, caused by elastocapillary densification, creates an additional bending moment in the direction of the tilt. This moment increases with the magnitude of tilt, thus acting as a destabilizing moment which is resisted by the bending stiffness of the CNT wall. Experimental results are independent of the orientation of the sample with respect to gravity.

We observe that relatively short walls densify and tilt but do not fold to the substrate. Therefore, these structures reach a static equilibrium under the influence of capillary forces. Taller walls densify, tilt, and then fold to the substrate. In our experiments where acetone was condensed from a heated vapor stream under otherwise ambient conditions, tilting happened over a duration of 2 s, and folding occurred abruptly within one frame of video (60 ms). Snapshots of the video are shown in Figure 2b.

The mechanism of folding is explained by considering the external (downward) force exerted on the CNT wall by the liquid, which causes the wall to buckle. We specify that the CNTs within the thin wall behave collectively as an elastic beam, with a force distributed around the perimeter of the wall. Further, due to the small contact angle between the liquid and the CNTs, and the small tilt angle, we approximate that this force acts along the axis of the CNTs. Consequently, CNT walls that are taller than a critical height fold to the substrate forming HA-CNT patches, and walls shorter than this height remain vertical and tilted after liquid evaporation. This critical height is known as the capillary buckling length (\( l_B \)). The capillary buckling length was previously defined as the minimum height of an elastic column, vertically submerged in a liquid, that buckles rather than pierces a liquid surface when the column is being pushed upward into the liquid–air interface. Therefore, the capillary buckling length is derived by equating the force due to the liquid surface tension on the column to the critical buckling load, such that

\[
l_B = \sqrt{\frac{E}{\gamma\gamma}}w
\]
Here, \( E \) is the elastic modulus of the densified CNT wall, \( \gamma \) is the solvent surface tension, \( t \) is the thickness of the wall (parallel to the folding direction), \( w \) is the width of the wall (perpendicular to \( t \)), and \( I \) is the second moment of area of the cross section (\( I = wt^3/12 \)). Thus, for rectangular walls, the capillary buckling length is proportional to \( t^{3/2} \) and is independent of \( w \).

Examination of a folded CNT patch shows that the wall bent near its base with a small radius curvature (Figure 2c), verifying that buckling occurred. There is no visual evidence of fracture or detachment from the substrate. This observation agrees with previous findings that individual CNTs,34 CNT bundles,35 and CNT forests36 buckle elastically according to a classical Euler model and withstand large strains associated with the small radius of curvature. When the liquid evaporates after buckling occurs, the receding meniscus “zips” the CNT wall onto the substrate, creating a flat patch that is held down by van der Waals forces. We also note that the arrows cause the side edges of the VA-CNT wall to taper inward during capillary densification. As a result, the HA-CNT patch is also tapered by a few degrees, resulting in a nonuniform thickness of the patch across the direction perpendicular to the CNTs. The thickness is best viewed from the edges that are perpendicular to the CNT alignment and by cross-sectioning using a focused ion beam (FIB), as shown in Figure 3.

Guided by the capillary buckling model, we engineer folding of VA-CNTs to HA-CNTs by specifying the line width of the catalyst pattern and by controlling the wall height \( h \), which is determined by the CNT growth time (50–100 \( \mu m/minute \)). Accordingly, we show in Figure 4b that the elastocapillary buckling length accurately predicts the folding behavior of CNT walls over 2 orders of magnitude of the scaling parameter \( l_B/h \). Here, walls with \( l_B/h > 1 \) fold to the substrate, whereas walls with \( l_B/h < 1 \) remain vertical. The direction of the arrows patterned at the end of each wall determines the folding direction with greater than 99% experimental certainty (measured from more than 100 folded samples), whereas walls without arrows obey the same stability criterion but fold in random directions. Arrays of CNT patches fabricated over the tested set of dimensions comprise individual patches with thickness from 300 nm to 2 \( \mu m \) and lateral areas from several \( \mu m^2 \) to mm\(^2\). Thus, by simply choosing the wall dimensions to be in the folding regime, HA-CNT patches can be fabricated over a wide range of length scales. The high packing density and lateral alignment of the CNTs within the folded patches are attractive attributes due to the anisotropic properties of CNTs.

Data from walls without arrows, as well as walls with different arrow geometries, are shown in Figure 1d and Supporting Information Figure S1. As the size of the arrows is increased, the centroid of the cross section is shifted farther from the center line of the wall. This leads to larger bending angles during densification. The steeper arrows also increase the lateral stiffness of the structures, thus making the structures more resistant to buckling. Thus, due to these competing effects, the accuracy of the present model based solely on Euler beam buckling theory is limited, and a more advanced model should be implemented for folding of thin-walled CNT structures with other cross-sectional shapes.

The self-directed nature of capillary folding can also be exploited to create unique multidirectional and multilayered CNT architectures. For example, arrays of rectangular HA-CNT “circuits” are made by patterning thin semicircular CNT walls that fold at right angles to one another (Figure 5a). Compound structures such as three thin walls connected in an “T” shape fold to create an arrangement including overlapping HA-CNTs with perpendicular orientations (Figure 5b).
transformation of the I-beam to a HA-CNT patch also tears the structure internally at the location of greatest lateral stress. This shows how the capillary folding method can overcome the serial nature of multistep printing or sequential patterning methods and achieve multidirectional architectures in a self-registered fashion.

Overall, the deterministic capillary folding behavior of CNTs demonstrates that the formation of complex patterns of laterally oriented nanostructures can be spatially “programmed” according to simple design rules. This method combines advantages of top-down fabrication in creating vertically aligned CNT patterns with deterministic locations and dimensions over large areas, with the self-directed nature of liquid wetting that guides nanostructures into ordered assembles. Further, while we only show HA-CNT patches with microscale dimensions, the underlying principles of capillary folding should be scalable to much smaller dimensions using higher resolution lithography to fabricate the CNT growth pattern. For example, a VA-CNT wall having $w = 0.5 \mu m$ and $h = 0.7 \mu m$ could form a HA-CNT patch of $\sim 50 \text{nm}$ thickness and $700 \text{nm}$ lateral span.

Practical advances from this study may be enabled by combining the highly anisotropic properties of CNTs with the mechanical flexibility offered by multidirectional HA-CNT films. For example, unidirectional films of HA-CNTs have been used as elements in transistors\textsuperscript{37} and electromagnetic polarizers,\textsuperscript{38} and both applications can benefit from the multidirectionality achieved by the capillary folding method. Moreover, methods of dry transfer printing\textsuperscript{23,24} could be applied to fabricate flexible and stretchable devices based on multidirectional HA-CNT elements, with improved design flexibility. In the future, anisotropic multidirectional NF networks may also achieve growth, differentiation, and stimulation of cells and tissues.\textsuperscript{40,41}

**ASSOCIATED CONTENT**

5 Supporting Information. Figure S1 showing a comparison of experimental results and analytical predictions of the folding transition for walls with different lengths. The experiment in the video is imaged using a CMOS camera (15 frames/s) attached to a stereomicroscope. During the experiment, the acetone vapor is condensing on the silicon substrate and the VA-CNT walls with different arrow geometries. The video shows that the VA-CNT tilts first then buckles and folds parallel to the substrate. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supplementary Information for

**Structurally Programmed Capillary Folding of Carbon Nanotube Assemblies**

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**Figure S1.** Comparison of experimental results and analytical predictions of the folding transition for walls with different lengths having: (a) no arrows; and (b) 90° arrows. These dimensions of these structures span two orders of magnitude of the aspect ratio \( t/w \).

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