FABRICATION OF COMPLEX SMART MICROSTRUCTURES BY CAPILLARY FORMING OF NANOSCALE FILAMENTS

Wei Lu [a)]
Mechanical Engineering, University of Michigan, Ann Arbor, Michigan, 48109, USA

Summary We present a mechanism for high-throughput fabrication of robust 3D smart microstructures with nanoscale filaments, which creates delicate and heterogeneous geometries in close proximity and over large areas. This method, called capillary forming, is based on our finding that condensation of liquid onto vertically aligned filaments, followed by evaporation, causes a deterministic transformation of the individual structures to intricate 3D shapes. We have exploited this mechanism to fabricate a diverse set of forms having controllable bends, twists, and re-entrant curves. Our mechanics model shows quantitatively that the lateral deflection and twisting can be controlled precisely by the pattern shape and the coupling strength among the filaments. Owing to their mechanical robustness and anisotropic electrical conductivity, these novel structures can be used as master molds for replication, responsive actuators, and electrically integrated sensors.

INTRODUCTION

Advances in miniaturized systems demand increasingly complex smart structures that are made in a precise, scalable, and cost-effective manner, and that exhibit multifunctional and responsive material properties. Growth of the integrated circuit and micro electro mechanical systems industries has fostered many manufacturing innovations including extreme ultraviolet and nanoimprint lithography, and fabrication of high-aspect-ratio and polymer microstructures. Nevertheless, it remains difficult to create non-planar, curved, re-entrant, and other freeform geometries at sub-millimeter scales; and existing methods of fabricating three dimensional (3D) microstructures suffer from tradeoffs among resolution, throughput, feature geometry, and heterogeneity. Nature uses self-assembly to create multifunctional hierarchical freeform geometries such as tissues and skeletal structures, that have inherent anisotropy that creates directional and responsive properties. We report a mechanism whereby ensembles of nanoscale filaments self-assemble into asymmetric bent or twisting aggregates by infiltration and subsequent evaporation of a liquid. With modelling and simulations, we reveal how the spatial distribution and mechanical coupling among the filaments can lead to diverse deflected or twisted microstructures spontaneously upon densification. The mechanism we discuss may present an enabling technique for scalable fabrication of smart filament assemblies at a wide range of length scales. The analysis also provides insight into analogous behaviors in nature where biological filaments interact with liquids.

A NOVEL MECHANISM OF CAPILLARY FORMING

We chose carbon nanotubes (CNTs) as an example, which have unique properties for smart materials and structures. Chemical vapor deposition (CVD) growth of CNTs enables efficient production of vertical "forest" microstructures having straight sidewalls and high aspect ratios, with dimensions ranging from micrometers to millimeters. Despite the exceptional properties of individual CNTs, the bulk properties of CNT forests are typically poor due to the low density of CNT growth, rendering them inadequate for most applications. Our process for creating dense and bent CNT microstructures is as follows (Fig. 1a). First, a film of iron catalyst is patterned by optical lithography on a silicon wafer substrate. Second, microstructures made of vertically aligned multi-wall CNTs (CNT "forests" as shown in Fig. 1b) are grown on the catalyst by atmospheric pressure thermal CVD. Next, a solvent such as acetone is condensed on the substrate. Due to capillary rise, the liquid that condenses onto the substrate is drawn into each CNT microstructure independently. Finally, the liquid is evaporated. During this process, the CNT forests are densified and shaped by local capillary action; we call this process "capillary forming" [1]. After capillary forming, the final shape of the densified CNT structure is held by intermolecular attractive forces, as well as mechanical interlocking due to the waviness of the aligned CNTs. In particular, CNT forests grown from semicircular patterns deflect laterally, creating bent micropillars (Fig. 1c).

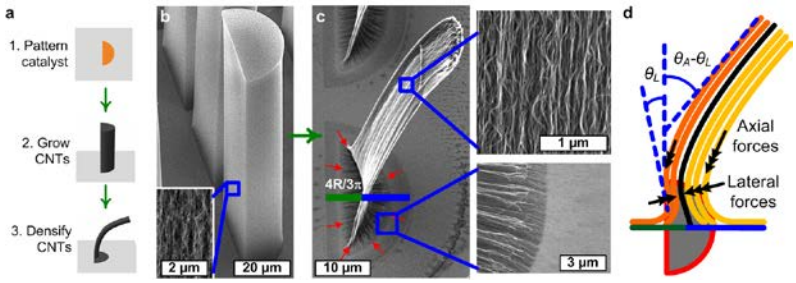

Fig. 1 Fabrication of asymmetric microstructures by elastocapillary densification: (a) process steps; (b) SEM image before densification, inset showing low-density vertically aligned morphology; (c) SEM image after densification, insets showing laterally aligned CNTs facing centroid of the base and high density vertical CNTs in the upper portion; (d) densification induced lateral and axial forces.

Since the collective properties of densely packed filament assemblies strongly depend on their morphology, the ability to predict and control the shape of the structures is critical. First, we find that the filaments at the base are flattened onto

[a)] Corresponding author. Email: weilu@umich.edu.

the substrate (Fig. 1c) due to capillary pressure on the perimeter of the microstructure. The lengths of flattened filaments are different, and the densified structure is located in close proximity to the centroid of the original cross section of the growth pattern. Further, the structure near the base is prone to bend toward the straight edge of the semicircle. In contrast, the upper portion of the structure, however, bends toward the opposite (curved) edge. Based on these observations, we identified two major effects contributing to the bending behavior (Fig. 1d) [2]. First, the filaments push against each other, introducing a distribution of lateral forces. The difference in population of filaments on both sides of the centroid results in the structure bending toward the straight edge. Second, the contraction of filaments creates a distribution of axial pulling forces that act asymmetrically on the upper portion of the forest. Based on the slip characteristics of filaments within the forest, this effect can lead to bending toward the curved or straight edge of the semicircle. The collective actions of the two effects determine the final bending angle of the densified structure. We have incorporated these mechanical effects and interface motion [3] into a continuum model, which allows predicting the morphology evolution of filament assemblies during evaporation.

RESULTS

Figure 2a shows representative results of elastocapillary densification of solid and hollow semi-cylindrical filament assemblies parametrized by $r=R_i/R_o$, with inner radius R_i and outer radius R_o. Our modeling curves and experimental data match each other. The total deflection is highly sensitive to r and a parameter k (between 0 and 1), which describes the significance of slip. When slip is absent (k=0), the densified structure always bends toward the straight edge (θ<0). With increasing r, the microstructure becomes a thin "C" shape and bends more. With slip among the filaments, the structure can bend toward the curved edge (θ>0). Take $k = 0.4$ as an example. At r=0, i.e., a semi-circular shape, the calculated bending angle is 13°. While the angle is -7° when k=0. This interesting transition can be understood as follows. When there is slip, those filaments far from the centroid lose grip first. As k increases, more filaments in the corners to the left of the red centroid lose grip (refer the inset in Fig.2a). As a result, those filaments to the right of the centroid win, and the resultant axial pulling force bends the structure toward the curved edge. This explains the possible reversal of the bending direction as r increases, and the further increase of the bending angle when k changes from 0 to 0.4. This effect becomes more important as r increases, because a greater proportion of the filaments are near the corner of the shape. Consequently, the net bending angle toward the curved edge is larger. The k =0.1 curve shows that when the interfacial strength of slip is fixed, changing the shape factor r can tune the bending from toward the straight edge to the curved edge. This intriguing behavior is captured by the experimental data. We have validated these trends in experiments with CNT microstructures. Figure 2b shows two sets of CNT structures, confirming the capability to tune the bending angle based on the initial pattern of filaments prior to elastocapillary densification. The different trends are created by varying the intensity of plasma etching of the CNTs in O_2/Ar prior to densification. The upper image matches the k =0.3 curve while the lower one is close to the k =0.1 curve. Understanding of the bending mechanism also allowed us to create complex arrangements of CNT structures as shown in Fig. 2c-e. These include flower-like architectures made from circular arrangements of structures that bend toward a common point; and large arrays of bending structures that resemble micro-hairs on the skin of insects. Notably, these structures range in size over two orders of magnitude, from a few microns to hundreds of microns in height. In addition to bending filament structures, we have designed and calculated catalyst pattern, predicted and demonstrated twisting microstructures as shown in Fig. 2f.

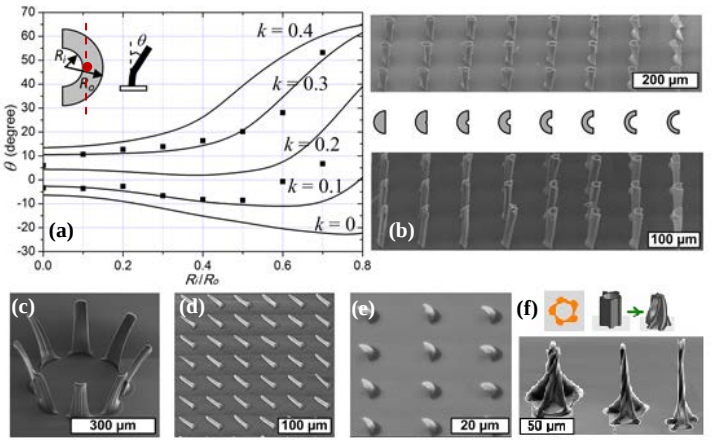

Fig 2. Representative results. (a) Bending angle changes as a function of R_i/R_o with different degree of slip. Solid squares for experimetnal data. (b) Precise control of bending angle by R_i/R_o. The two sets represent different amount of slip. Each image shows three identical rows to verify repeatibility. (c) "Blooming flowers" of structures bending toward the curved edge of the semicircle. (d) Large arrays of bending structures. (e) Short bending CNT structures (f) CNT micro-helices with deterministic handedness and pitch.

CONCLUSIONS

We introduced a mechanism by which nanoscale filaments form laterally bent assembles during elastocapillary densification of filament assemblies. The coupling of capillary effects and internal sliding among filaments can produce a rich pattern of complex morphologies. These findings can enable a class of approaches to form complex and biomimetic smart structures.

References

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