Capillary bending of Janus carbon nanotube micropillars†

Sameh Tawfick,†a A. John Harta and Michaël De Volder*b

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We present a scalable process for the fabrication of slanted carbon nanotube micropillar arrays by inclined metal deposition and capillary self-assembly. Local control of the micropillar angle from vertical to nearly horizontal is achieved, and is explained using a finite element model. These structures may be useful for microscale contacts and anisotropic smart surfaces.

The advent of nanotechnology has fostered the development of a new generation of materials and surface textures mimicking the behaviour of natural smart materials.1–8 For example, natural dry adhesives, photonic crystals and hydrophobic surfaces rely on anisotropic hierarchical surfaces having intricate microscale geometries along with nanoscale topologies.9–17 More specifically, the feet of gecko lizards and certain insects are covered with branching microscale fibres that have nanoscale hairs at their tips to provide compliant contacts. Further, the hairs are slanted in order to provide directional adhesion, which facilitates locomotion on vertical walls.

Scalable fabrication of 3D surface textures mimicking these inclined micro- or nano-pillars remains a major challenge in microfabrication.3 There has been much recent effort in developing arrays of non-vertical micropillars by inclined lithography, micromolding, glancing angle deposition, electrodeposition and directed mechanical deformation by thermal stresses.5,18–21 Here, we present a new approach for the fabrication of inclined micropillars by capillary driven deformation of carbon nanotube micropillars. The process relies on chemical vapour deposition (CVD) of vertically aligned (VA-) CNTs,22–24 followed by an inclined metal coating step to form Janus pillars, and finally, capillary self-assembly to simultaneously densify and tilt the pillars.25–29 The resulting inclined micropillars consist of densely packed aligned CNTs, which is conducive to mimicry of smart natural materials. Further, the nanoscale topology of the constituent CNTs is potentially advantageous for both dry adhesion purposes, as it increases van der Waals interactions, and engineering of wetting properties.1,5,30,31

Fabrication process

As illustrated in Fig. 1, the fabrication process comprises three major steps. First, CNT pillars are made by thermal CVD.22 In this step, a catalyst layer of 10 nm Al2O3 and 1 nm Fe is patterned on a silicon wafer using lift-off processing. Next, the substrate with catalyst is transferred to a tube furnace where at 775 °C CNTs are grown under a flow of 100/400/100 sccm C2H4/H2/He. Importantly, the nanotubes self-support one another to form vertically aligned assemblies which result in vertical “extrusion” of the catalyst pattern in the form of CNTs.23 For example, patterning the catalyst in circles results in vertical micropillars with circular cross-sections as shown in Fig. 1A. Note that the thin CNT pillars shown in Fig. 1A are not perfectly straight after growth, which induces variation in the bending angle in spite of the high uniformity of metal deposition.

Analogous to fabrication of Janus polymer pillars (e.g., pillars coated on one side or with two different halves),19 we then deposited metal onto the CNT pillars by inclined e-beam evaporation. In this step, the substrates are coated with 5 nm Ti and 40 nm Au. Due to shadowing effects, only one side of the pillars gets coated as shown in Fig. 1B. The inset shows the transition from the coated to the bare side of a pillar, where the metal coats the individual CNTs within the pillar.

![Fig. 1](A) CNT micropillars grown by CVD on a silicon substrate. (B) CNT pillars after oblique Au evaporation, where the left side of each pillar is coated with Au. (C) Au-coated CNT pillars after capillary self-assembly, which caused shrinkage and directional bending of the CNT pillars.
In previous studies, the bending of Janus micropillars has been controlled, for instance, due to differences in thermal expansion between the core material and the coating, due to stresses induced during the coating deposition, or by e-beam irradiation after deposition.\textsuperscript{5,31,32,33} When bending is induced by thermal contraction, deposition at significantly elevated temperatures is required; and when residual stresses are used, fine control of the coating deposition parameters is required.

Instead of introducing thermal stress, our process uses inclined deposition of a thin coating onto the CNTs to induce mechanical asymmetry that causes the pillars to tilt upon capillary densification of the pillars. The densification of VA-CNTs upon liquid infiltration and subsequent evaporation is based on elastocapillary interaction between CNTs and a wetting liquid.\textsuperscript{25,28,29,35} More precisely, capillary action of an organic solvent (e.g., acetone) causes a re-arrangement of the CNT network as it infiltrates and evaporates from the structure. Capillary forces bundle the CNTs into a more tightly packed configuration, causing an overall shrinkage of the CNT pillars. Importantly, the Au layer on one side of the pillars prevents slipping of the CNTs among each other during densification and therefore presents a higher resistance to capillary densification. As will be discussed in more detail later, the difference in CNT interactions between the bare side and the Au-coated side drives the directional bending of the pillars as shown in Fig. 1C. This relatively simple process enables fine control of the inclination angle, and at the same time, the capillary densification of the CNT pillars enhances their mechanical robustness.\textsuperscript{34}

In our experiments, the capillary self-assembly step was performed by attaching the CNT sample to a perforated aluminum sheet and inverting it over a beaker containing boiling acetone. As the upward vapour flux meets the cold substrate, it condenses and causes capillary self-assembly of the CNTs during infiltration and evaporation.\textsuperscript{34} This way, controlled deposition of acetone was achieved without pooling the substrate, enabling fabrication of large arrays of structures without coupling due to capillary bridges. We call this process “capillary forming”.\textsuperscript{29}

**Discussion**

The structure of the slanted Janus CNT pillars after capillary forming is shown in Fig. 2A–D. The base of the pillars exhibits CNT bundling and folding into a densely packed geometry. This folding of CNTs at the base plays a key role in the deflection of the pillars. However, the height of the pillars has little influence on the inclination angle. For instance, Fig. 2A and B show that pillars with the same cross-section and same metal deposit bend the same amount, regardless of the CNT pillar height. The importance of the CNT folding at the base of the pillar is further supported by the observation that, if the base of the pillars is not coated, for instance due to shadowing as in the case of Fig. 2E, the pillars will not bend. Finally, it is interesting to observe that the pillars remain straight above the base (see Fig. 1–3). This further suggests that the directional motion of each CNT pillar is driven by asymmetric deformation localized among the CNTs at the base.

The cross-sectional dimensions of the pillars influence the bending angle. This is illustrated in Fig. 3A which shows an array of pillars with identical height and Au thickness but varying cross-sectional dimensions. We observed that pillars with diameter greater than \(~100\,\mu\text{m}\) remain vertical on the silicon substrate after densification, while pillars of \(5\,\mu\text{m}\) diameter tilt up to \(90^\circ\) and align horizontally on the substrate under the same conditions (Fig. 3D–F). In between these limits, the bending angle depends on the initial diameter of the CNT pillar (Fig. 3A). Also, the shape of the pillar influences the deformation. While cylindrical pillars receive a gradient in metal deposition over half of their circumference (due to the changing view factor relative to the deposition source), rectangular pillars receive metal deposition only on the side that faces the source. As a result, rectangular pillars have higher bending angles as shown in Fig. 3E. Square pillars with \(5\,\mu\text{m}\) side length are folded and become almost parallel to the substrate.

To understand the mechanism of directional deformation, we consider the capillary pressure of the liquid meniscus formed within the CNT microstructures. As the liquid evaporates, the capillary forces apply inward lateral pressure on the pillars and shrink their cross-sections.\textsuperscript{34,36} First, we hypothesized that differences in contact angle between the solvent and the Au-coated surface and the bare CNT surface could account for the observed tilting. However, measurements showed that the contact angle of acetone on CNTs and Au is comparably small and close to \(5^\circ\). Therefore, changes in contact angle due to the Au coating do not cause the observed bending.

Instead, we consider the changes in the flexural rigidity (\(\text{EI}_{\text{CNT}}\)) of individual CNTs due to Au coating and the interactions among CNTs in the pillars. Here, \(\text{EI}_{\text{CNT}} \approx 1\,\text{mN nm}^2\) (for a CNT with...
Here, certain dimensions. The calculated elastocapillary length of bare and the capability of the surface tension forces to bend CNT structures of characteristic width ($r_0 = 20 \text{ nm}$) is the liquid surface tension (mN m$^{-1}$) and $b$ is the CNT characteristic width (e.g. diameter, nm). This provides an estimate of the capability of the surface tension forces to bend CNT structures of certain dimensions. The calculated elastocapillary length of bare and Au-coated CNTs is approximately 1 $\mu$m and 10 $\mu$m, respectively. The elastocapillary height of 10 $\mu$m of the Au-coated CNTs predicts that they should shrink and aggregate into one bundle at a height of 10 $\mu$m from the substrate which is not observed in our experiments. We see little to no deformation of the Au-coated CNTs having length $>10$ $\mu$m. Therefore, the Au-induced capillary bending cannot be explained by the increase in flexural rigidity alone.

We hypothesized that Au coating is significantly increasing the shear modulus of the CNT forest by reinforcing the CNT–CNT contacts. We investigated this by building a non-linear large deformation finite element (FE) model (Abaqus) to study the effect of contact and slip among Au-coated CNTs as densification occurs. As shown in Fig. 4, a model consisting of a pair of vertical cantilever beams is implemented. The right beam represents an individual bare CNT and the left pillar an Au-coated CNT. These represent the opposite sides of the Janus metal-coated pillar. The Au-coated CNT has a higher flexural rigidity as discussed earlier. The beams in this model represent the CNTs near the substrate where we observe significant deformation that causes bending of the microstructure (cfr. Fig. 2D). In the Abaqus simulation, equal uniform capillary pressure is applied on the two beams laterally inwards. The pressure direction is normal to the beams and follows their deformation.

Using this framework, we consider two limiting cases. In the first case, the CNTs are allowed to slide against each other as they come in contact. This simulates a hypothesis in which Au does not change the interaction between CNTs. In this case, the model predicts that the CNTs deflect, come into contact, and remain straight. In the second case, the contact problem is programmed to prevent sliding once the surfaces of the CNTs come in contact. We observe that the CNTs deform, and bend towards the side of the uncoated CNT. Therefore, this model predicts the bending of the pillars observed experimentally (Fig. 1–3). Note that after coming into contact, the CNTs form a straight line above the initial contact point (Fig. 4). This is in agreement with our experimental results which show that the bending angle does not depend on the pillar length (Fig. 2A and B).

Based on the results of the finite element model, we conclude that Au coating changes the interconnections among the CNTs in the pillars. During capillary densification, the relative sliding of CNTs as they laterally deform is crucial for the pillars to laterally shrink. As shown in Fig. 3F and G and 4, the Au deposition connects the CNTs thus preventing their relative sliding and hence restricts the shrinkage of the Au-coated portion of the structure. Owing to the Au induced change in flexural rigidity, highly asymmetric shear strains are developed in the vicinity of the Au-coated side of the pillars. Because the penetration depth of the Au coating is small (and does not depend on the pillar width), the shear stresses are localized near the Au-coated side. Consequently, the bending angle increases for smaller pillars as observed in Fig. 3A–C.

The influence of the Au coating on the structural stiffness is also illustrated in an experiment where the Au layer is etched away, and subsequently the CNTs are capillary self-assembled a second time (Fig. 3F and G). In this case, the Au-coated side initially retains its full width during capillary self-assembly (Fig. 3F), but when the Au coating is removed, the CNTs lose the enhanced connectivity provided by the Au coating (cfr. Fig. 4). Therefore, during the second capillary self-assembly process, the pillar contracts to approximately half its initial width (Fig. 3G).

Finally we would like to compare our process and findings to other methods for capillary densification of CNT forests and
microstructures that were not coated with metals, including by immersion in liquids \(^{25,28,37}\) and condensation of liquids. \(^{26,29,38}\) We have previously shown that self-directed capillary densification (capillary forming) initiated by condensation enables directional bending and folding of individual CNT pillars based on the asymmetry of the pillar cross-section. The approach presented in this paper enables fine control of the CNT pillar bending angle; however, a disadvantage is that the bending direction is dictated by the inclined metal deposition which is constant over the entire substrate. Therefore, multi-directional deformation \(^{28,29}\) is not possible with this process. Present experiments were performed on \(8 \times 15\) mm samples, and the spacing of the pillars is limited by the shadowing effect illustrated in Fig. 2E. Additional experiments were conducted with more closely spaced pillars and smaller deposition angles relative to the substrate. However, this did not introduce enough anisotropy to induce bending, as shown in ESI Fig. S1†.

Nevertheless, the structures fabricated by the present method are potentially attractive for a number of potential applications. First, the ability to fold CNTs horizontally has application in interconnects, resonators, and other microelectronic systems. \(^{5,17,19,28}\) For these applications, the Au layer can optionally be etched away as shown in Fig. 3G. A further advantage of the capillary self-assembly used in our process is that it enhances the robustness of CNTs, and therefore enables lithographic post-processing for integration in contact probe arrays and other CNT MEMS devices. \(^{25,27,38,41}\) Another field of application could be the fabrication of anisotropic biomimetic smart materials mentioned in the introduction, which include dry adhesives and surfaces with anisotropic wetting properties. \(^{3,16,17,33}\) Both these applications would profit from anisotropic surface design due to both the slanted organisation of the micropillars and their Janus coating. \(^{19}\)

The nanoscale topography of the nanotubes could enhance dry adhesive contact \(^1\) and influence wetting properties. \(^3\) And, the metal coating could add complementary sensing functionality such as by surface enhanced Raman spectroscopy. \(^{42}\)

Conclusions

Recent developments in the study of biologic smart surfaces and nanoscale fabrication are converging towards new hierarchical anisotropic materials. This paper presents a new fabrication and simulation method for such anisotropic materials relying on oblique metal deposition on CNT pillars, followed by capillary self-assembly. This process enables controlled directional bending, over a range of nearly 90°. We envision that the combined bending and Janus coating of the CNT pillars together with their nanoscale topography could enable design of new multi-functional surfaces.

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Notes and references


