

Video Article

Fabrication, Densification, and Replica Molding of 3D Carbon Nanotube Microstructures

Davor Copic¹, Sei Jin Park¹, Sameh Tawfik¹, Michael De Volder², A. John Hart¹

¹Mechanosynthesis Group, Department of Mechanical Engineering, University of Michigan

²IMEC, Belgium

Correspondence to: A. John Hart at ajohnh@umich.edu

URL: <https://www.jove.com/video/3980>

DOI: [doi:10.3791/3980](https://doi.org/10.3791/3980)

Keywords: Mechanical Engineering, Issue 65, Physics, Carbon nanotube, microstructure, fabrication, molding, transfer, polymer

Date Published: 7/2/2012

Citation: Copic, D., Park, S.J., Tawfik, S., De Volder, M., Hart, A.J. Fabrication, Densification, and Replica Molding of 3D Carbon Nanotube Microstructures. *J. Vis. Exp.* (65), e3980, doi:10.3791/3980 (2012).

Abstract

The introduction of new materials and processes to microfabrication has, in large part, enabled many important advances in microsystems, lab-on-a-chip devices, and their applications. In particular, capabilities for cost-effective fabrication of polymer microstructures were transformed by the advent of soft lithography and other micromolding techniques^{1,2}, and this led a revolution in applications of microfabrication to biomedical engineering and biology. Nevertheless, it remains challenging to fabricate microstructures with well-defined nanoscale surface textures, and to fabricate arbitrary 3D shapes at the micro-scale. Robustness of master molds and maintenance of shape integrity is especially important to achieve high fidelity replication of complex structures and preserving their nanoscale surface texture. The combination of hierarchical textures, and heterogeneous shapes, is a profound challenge to existing microfabrication methods that largely rely upon top-down etching using fixed mask templates. On the other hand, the bottom-up synthesis of nanostructures such as nanotubes and nanowires can offer new capabilities to microfabrication, in particular by taking advantage of the collective self-organization of nanostructures, and local control of their growth behavior with respect to microfabricated patterns.

Our goal is to introduce vertically aligned carbon nanotubes (CNTs), which we refer to as CNT "forests", as a new microfabrication material. We present details of a suite of related methods recently developed by our group: fabrication of CNT forest microstructures by thermal CVD from lithographically patterned catalyst thin films; self-directed elastocapillary densification of CNT microstructures; and replica molding of polymer microstructures using CNT composite master molds. In particular, our work shows that self-directed capillary densification ("capillary forming"), which is performed by condensation of a solvent onto the substrate with CNT microstructures, significantly increases the packing density of CNTs. This process enables directed transformation of vertical CNT microstructures into straight, inclined, and twisted shapes, which have robust mechanical properties exceeding those of typical microfabrication polymers. This in turn enables formation of nanocomposite CNT master molds by capillary-driven infiltration of polymers. The replica structures exhibit the anisotropic nanoscale texture of the aligned CNTs, and can have walls with sub-micron thickness and aspect ratios exceeding 50:1. Integration of CNT microstructures in fabrication offers further opportunity to exploit the electrical and thermal properties of CNTs, and diverse capabilities for chemical and biochemical functionalization³.

Video Link

The video component of this article can be found at <https://www.jove.com/video/3980/>

Protocol

1. Catalyst Patterning

1. Acquire a (100) silicon wafer with a 3000Å thick silicon dioxide layer, with at least one polished side. Alternatively, you may acquire a bare silicon wafer and grow 3000Å silicon dioxide on the wafer. All processing described below is done on the polished side of the wafer.
2. Spincoat a layer of HMDS at 500rpm for 4s, then at 3000rpm for 30s. HMDS promotes adhesion between the wafer and the photoresist.
3. Spincoat a layer of SPR-220-3 at 500rpm for 4s, then at 3000rpm for 30s.
4. Bake the wafer on a hotplate at 115°C for 90s.
5. Using the desired mask for catalyst patterning, expose the wafer to UV light with an irradiance of 20 mW/cm² at 405 nm for 6s in hard contact mode. 1.6) Bake the wafer on a hotplate again at 115°C for 90s (post exposure bake).
6. Develop the exposed photoresist for 60s using AZ-300 MIF developer.
7. Rinse the wafer for 60s in DI water.
8. Deposit 10nm Al₂O₃ followed by 1nm Fe by e-beam evaporation or sputtering.
9. Manually scribe and break wafer into pieces approximately 20×20 mm or smaller.
10. Perform lift-off of the photoresist by soaking the wafer pieces in a 1L beaker containing 100ml of acetone, while the beaker is placed in an ultrasonic bath at power 6 for 8min (CREST Ultrasonics 1100D).
11. Dispose and replace the acetone and sonicate again with the same settings.

12. Transfer the wafer pieces to a beaker with isopropanol (IPA), then soak for 2min.
13. Remove the wafer pieces from the IPA individually using tweezers. Dry each piece with a gentle nitrogen stream using a handheld nozzle.

2. CNT Growth

1. Acquire a bare (or oxide-coated) silicon wafer and manually scribe and break a piece with dimensions approximately 22×75 mm. This "boat" will be used to support and load the catalyst-coated wafer pieces into the tube furnace. The boat is very useful for holding the wafer pieces during loading and unloading, but does not play a role in the growth process. In principle the boat may be any material that is chemically and thermally stable under the CNT growth conditions.
2. Place a desired number of catalyst-coated wafer pieces (growth substrates) on the boat, 30mm from the leading edge.
3. Load the boat with growth substrates into the tube. Push the boat into the tube such that the leading edge is located 30mm downstream of the furnace thermocouple, using a stainless steel or quartz push rod. This 30mm position is the "sweet spot" which gives the highest CNT growth rate in our furnace. It will be necessary to determine this position for the user's apparatus, depending on the user's apparatus and objectives (e.g., maximization of CNT growth rate or density).
4. Connect the end caps, sealing the tube. Care should be taken to not disturb the position of the boat or the patterned silicon pieces. Note: CNT growth is highly sensitive to position inside the tube.
5. Flush the quartz tube with 1000sccm of helium for 5min at room temperature.
6. While flowing 400sccm of hydrogen and 100sccm of helium, ramp the temperature to 775°C in 10min, and then hold the flows and temperature for 10min. This step causes the film to chemically reduce from iron oxide to iron, and to dewet into nanoparticles.
7. Change the hydrogen flow rate to 100sccm and the helium flow rate to 400sccm, while adding 100sccm of ethylene and maintaining the furnace at 775°C to grow CNTs. The height of the CNTs is controlled by the duration of this step.
8. To stop CNT growth and cool the sample, manually slide the quartz tube downstream until the catalyst chips are located approximately 1cm downstream of the furnace insulation. Use care to maintain the same flows and furnace set point temperature as in the previous step, for 15 minutes.
9. Flush the tube with 1000sccm of helium for 5min, prior to retrieving the samples, and turning the furnace off.

3. CNT Densification

1. Apply a piece of double-sided tape to an 0.8mm thick aluminum mesh with 6.25mm diameter holes. Make sure the mesh is larger than the opening of a 1L beaker and the tape is approximately centered on the mesh.
2. Mount the silicon wafer piece with CNTs on the tape so the CNT microstructures are facing upward.
3. Pour 100ml acetone into a 1L beaker and place the beaker on a hot plate inside a fume hood. Set the hot plate to achieve a surface temperature of 110°C. Wait until the acetone starts boiling. We note that, on our hotplate, a setting of 150°C was required to achieve 110°C on the surface. The boiling point of acetone is much lower (approx. 56 °C) but we found that the elevated temperature allowed the acetone to boil more quickly, and heated the sidewalls of the beaker, preventing condensation within the beaker.
4. Place the aluminum mesh on the beaker such that the mounted sample is facing downwards.
5. Note any rapid fluctuations in the vapor front rising up the side of the beaker and adjust the fume hood sash level to stabilize the vapor front.
6. Once the vapor front approaches the top of the beaker, observe the apparent color changes on the surface of the silicon substrate. Rainbow-like patterns will appear and sweep across the entire surface. This signifies a thin film of solvent forming on the surface when the vapor comes into contact with the cold surface.
7. Once enough solvent has been deposited, pick up the mesh and without changing the orientation of the sample, hold it away from the boiling solvent until the deposited solvent has evaporated away. The amount of time is determined empirically based on the size and spacing of the CNT structures. This is addressed further in the discussion.
8. Remove the mesh from the beaker, and carefully peel off the sample from the double-sided tape, using a razor blade. Utmost care should be taken at this step as it is easy to break the sample during removal.

4. CNT Master Mold Fabrication

1. Pool SU-8 2002 on the densified CNT microstructures. Spin the sample at 500rpm for 10s, then at 3000rpm for 30s.
2. Bake the sample at 65°C for 2 min and then at 95°C for 4 min.
3. Expose the sample to UV light with an irradiance of 75mW/cm² for 20s.
4. Bake the sample again at 65°C for 2 min, then at 95°C for 4 min.

5. Replica Molding

1. If replicating delicate structures, place the master in a desiccator along with a glass vial of 100μL of (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane at 400mTorr for 12h.
2. Mix a total of 1g of PDMS (Sylgard 184), with a ratio of 10:1 monomer:cross-linker. For microstructures with a base size of a few micrometers and an aspect ratio of 10 or more use a ratio of 8:1.
3. Place the CNT master in an aluminum foil dish, and pour PDMS into the dish until the sample is submerged.
4. Place the sample in vacuum and degas at 400mTorr for 15 min. Once bubbles begin to form in the PDMS (typically after about 3 minutes) periodically increase the pressure rapidly to burst large bubbles.
5. Cure the negative at 120°C for 20 min. If the sample contains HAR structures, cure at 85°C for 5h.
6. Once cured, peel back the aluminum foil and separate the master from the soft PDMS negative by hand.
7. If replicating delicate structures, place the negative in a desiccator along with a glass vial of 100μL of (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane at 400mTorr for 12h.
8. Pour SU-8 2002 into the PDMS negative and degas at 400mTorr for 10min.

9. Bake the sample (SU-8 filled negative) at 65°C for 4min, then at 95°C for 6h to evaporate the solvent from the thick layer of SU-8.
10. Expose the sample to UV light with an irradiance of 75mW/cm² for 20s and bake again at 65°C for 4min and then at 95°C for 8min.
11. Last, manually demold the SU-8 replica from the PDMS negative.

6. Representative Results

Representative as-grown CNT pillar arrays along with their densified shapes are shown in Figure 4 (image modified from De Volder *et al.*⁴). HAR pillars with thicknesses of 10µm or smaller have progressively reduced straightness, which is further reduced during densification. Densification of semicircular pillars has been shown to result in uniform bent pillars over large areas (Fig. 4c). SU-8 infiltration occurs in between and inside CNT microstructures, for structures with spacing of 30µm or below a thin film of SU-8 may remain between structures. Photographs of critical steps in the replication process are shown in Figure 5, while SEM images comparing the replicated microstructures to their replicas on various scales are shown in Figure 6 (image modified from Copic *et al.*⁵). Current limits, in terms of structure formation, including twisted structures (image modified from De Volder *et al.*⁴), high aspect ratio walls, and re-entrant structures are shown in Figure 7 (image modified from Copic *et al.*⁵).

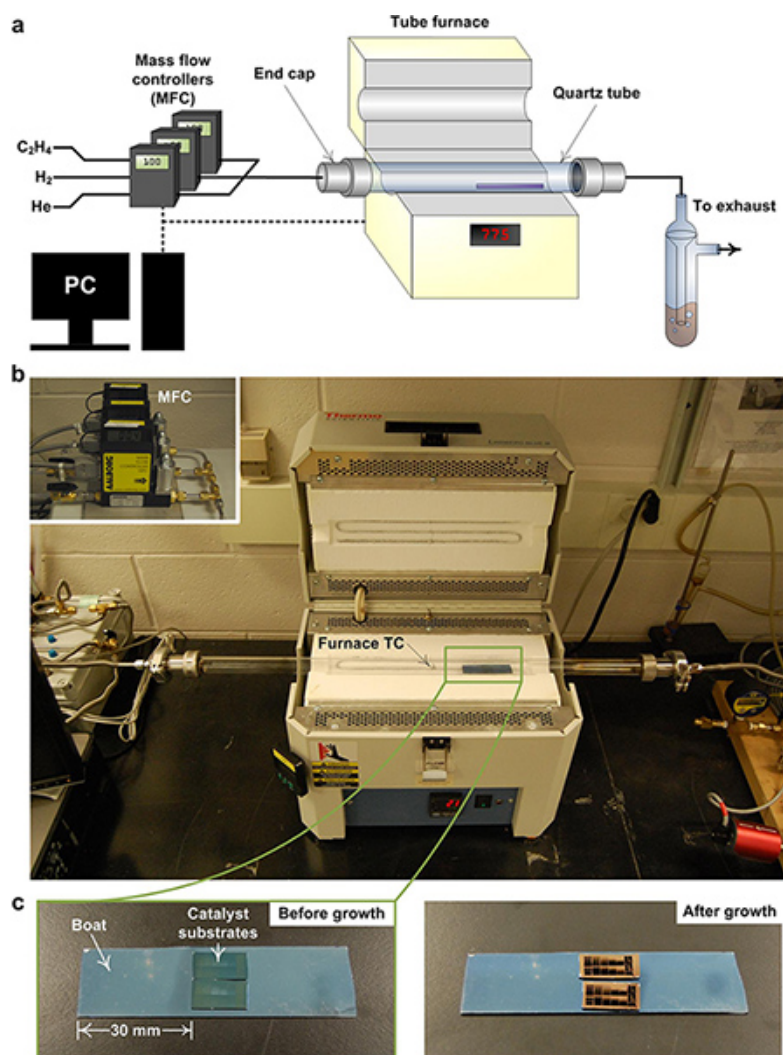


Figure 1. Tube furnace setup for growth CNT growth. (a) System schematic. (b) Tube furnace (Thermo-Fisher Minimate), with cover open to show silicon boat inside sealed quartz tube. (c) Silicon boat with samples, shown before and after growth. [Click here to view larger figure.](#)

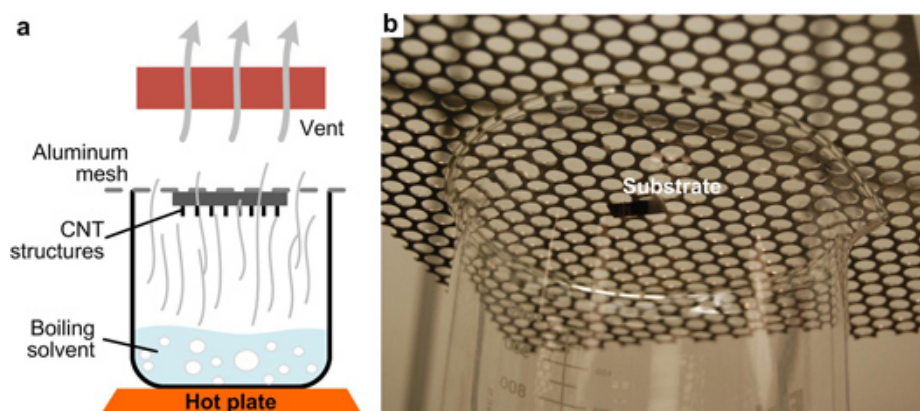


Figure 2. (a) Schematic of beaker setup for controlled condensation of solvent vapor onto CNT microstructures (image modified from De Volder *et al.*⁶). (b) CNT sample substrate attached to aluminum mesh over boiling acetone.

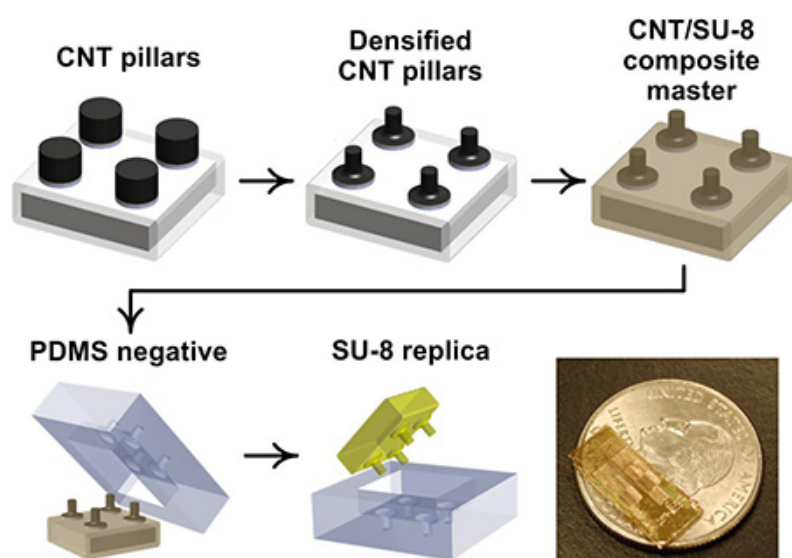


Figure 3. Process flow for replica molding of CNT microstructures, and image of representative replicated microstructure array compared to U.S. quarter dollar coin.

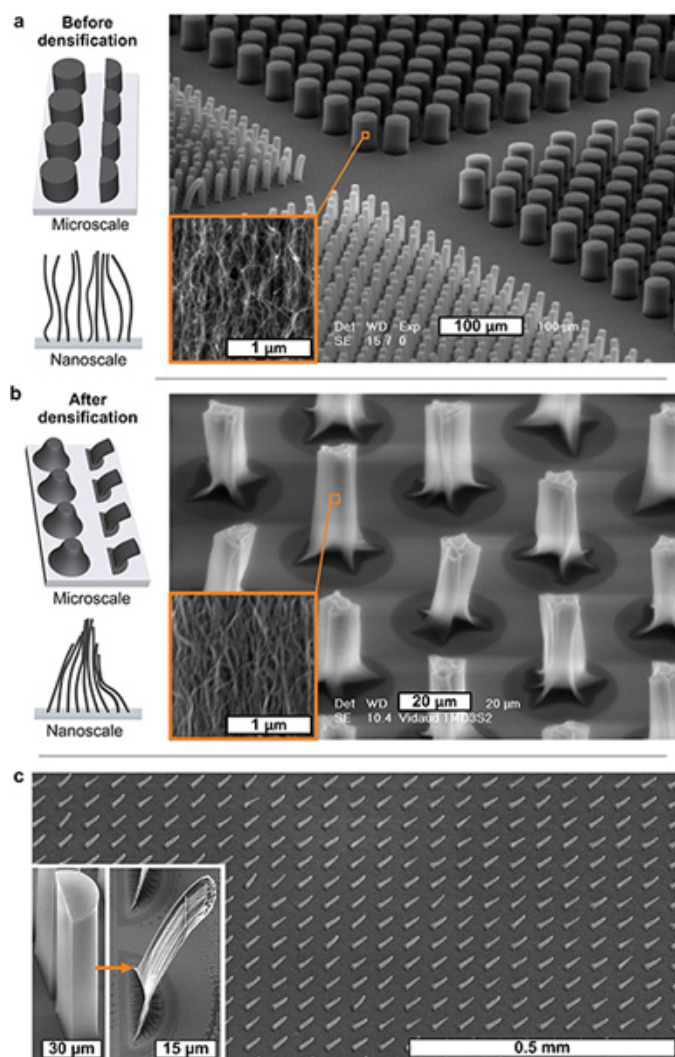


Figure 4. Exemplary CNT microstructures before and after capillary forming. Schematic and SEM images of array of cylindrical CNT pillars (a) before capillary forming, and (b) after capillary forming (image modified from De Volder *et al.* ⁶). Insets show alignment and density of CNTs. (c) Semicylindrical CNT pillars density and tilt during capillary forming, forming inclined beams (image modified from Zhao *et al.* ⁷). [Click here to view larger figure.](#)

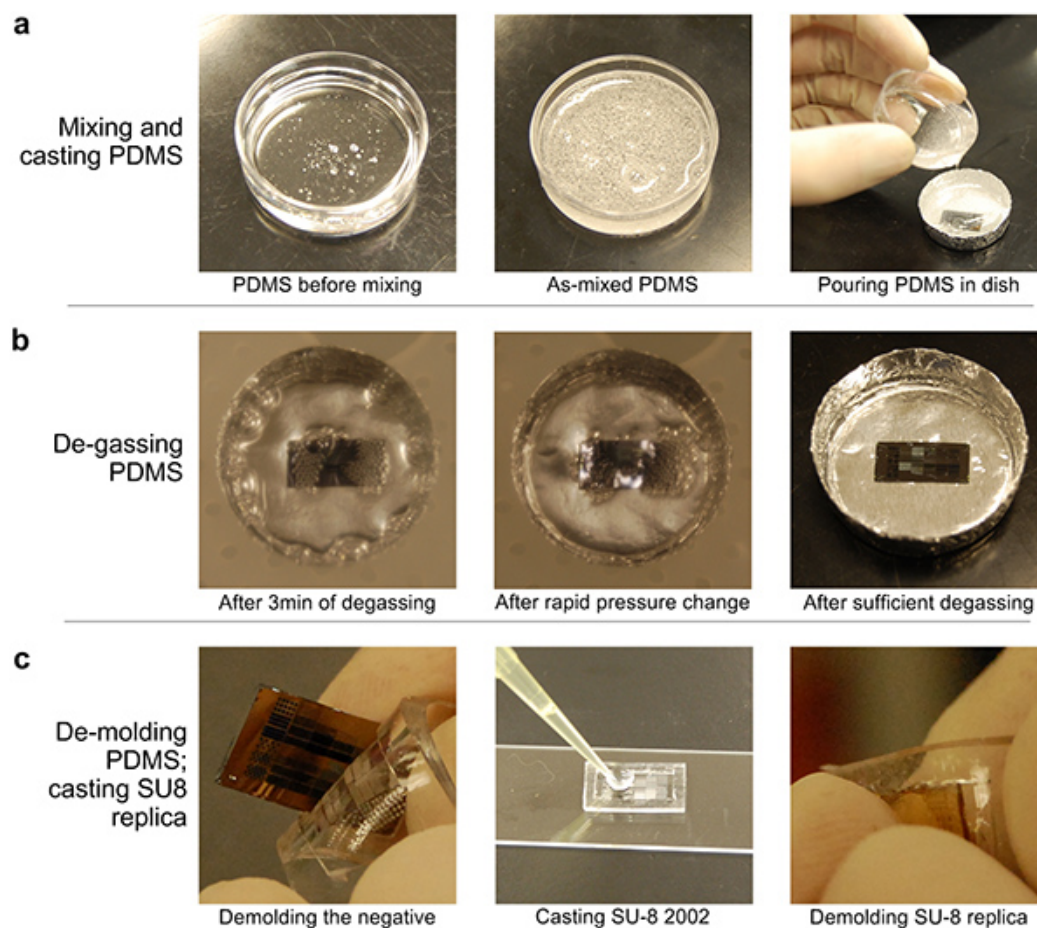


Figure 5. Key steps of CNT negative mold fabrication and replica casting. (a) Casting of PDMS negative mold. (b) Degassing of the negative mold. (c) Manual demolding of the negative, and casting of the SU-8 replica.

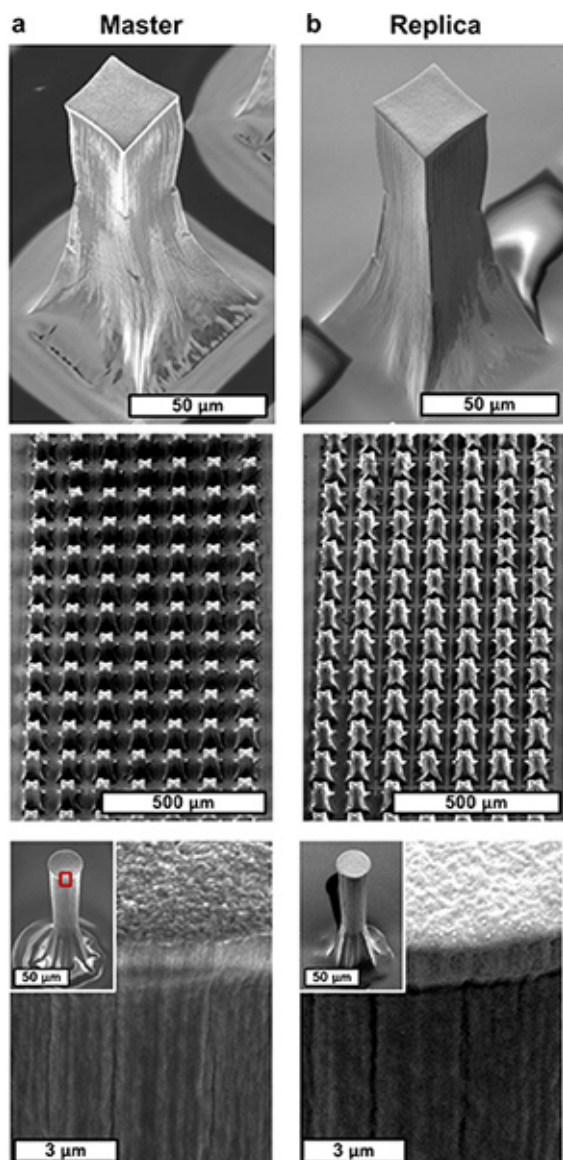


Figure 6. Comparison of (a) CNT/SU-8 master and (b) replica micropillar structures showing high fidelity replication of micro-scale shape and nanoscale texture (i.e., sidewalls and top surface), over a large area (image modified from Copic *et al.*⁵). [Click here to view larger figure.](#)

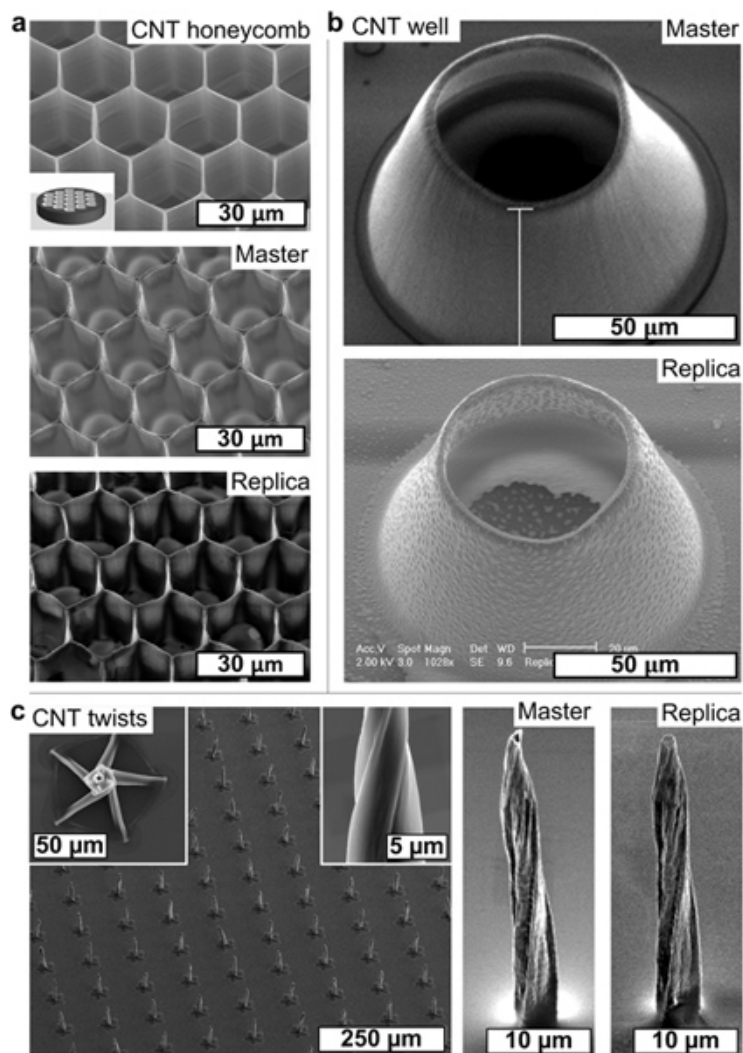


Figure 7. High-aspect-ratio (HAR) and re-entrant CNT microstructures and their polymer replicas. (a) Densified CNT honeycomb with corresponding SU8-CNT master and SU8 replica. (b) Master and replica of sloped CNT microwell (image modified from Copic *et al.* ⁵). (c) Densified twisted CNT micropillars, with master and replica of individual structure (image modified from De Volder *et al.* ⁴). The honeycombs in (a) have wall width of 400 nm and height of 20 μm. [Click here to view larger figure.](#)

Discussion

Lithographic patterning and preparation of the CNT catalyst substrates is straightforward and repeatable; however, achieving consistent CNT growth requires careful attention to how the height and density of CNT forests are impacted by the ambient humidity and the condition of the growth tube. In our experience, patterns larger than 1000 μm² are less sensitive to small fluctuations in the processing conditions. Further, the density of the patterns plays affects the growth density and height⁶. The growth density and height are larger for patterns with fill fraction (total area of catalyst divided by total substrate area) greater than approximately 20%. Also, it is important vital to keep the growth tube clean and bake out the tube between consecutive growths to remove accumulated carbon deposits. Tube baking is performed by heating the tube for 30 minutes at 875°C with 100 sccm of air flow. Furthermore, the CNT growth rate depends on the temperature, gas composition, and residence time of the gas in the furnace. Thus, it is often necessary to empirically find the "sweetspot" in any growth system, and the placement of the samples in the procedure noted here is based the sweetspot for our tube furnace and process parameters.

The most important properties of our CNT forests for densification and subsequent master mold formation are their alignment, packing density, and adhesion to the substrate. When CNT microstructures are etched by brief exposure to oxygen plasma, the top "crust" of tangled CNTs is removed. This crust constrains the CNT forest laterally, and therefore removing the crust enables greater densification of the CNTs, and increases the amount of slip that occurs among the CNTs during the densification step. Also, the CNT diameter can be tuned by the catalyst film thickness, and by the annealing conditions that precede injection of the hydrocarbon source to the CVD furnace⁹. By tuning the annealing conditions and optionally etching the CNTs, we have tuned to the densification factor from approximately 5X to 30X⁶. And, the adhesion of the CNTs to the substrate is enhanced by rapidly cooling the substrates in the growth atmosphere immediately after the conclusion of the programmed growth time. In this case, the furnace is enclosure is opened and the heater power is turned off while the growth gas mixture is still flowing through the furnace tube. These details are discussed thoroughly in our other publications cited herein.

In order to achieve consistent CNT densification, one must avoid excessive solvent condensation on the substrate. Excessive condensation causes the CNT structures to be flooded, which can warp, flatten, or delaminate HAR microstructures. The required amount of condensation to fully densify the CNTs depends on both the height and density of the microstructures. In our practice, the amount of solvent condensation is monitored by counting the number of "waves" of solvent that sweep across the substrate. The colorful waves represent optical interference patterns due to the thin film of condensed liquid on the substrate. For typical microstructures with dimensions 10-100 μm , between 1 and 5 waves are required in our setup. Therefore, the amount of solvent in the beaker may be chosen accordingly, or the sample may be removed from the beaker after the desired number of waves has passed.

Master mold formation is highly dependent on SU-8 infiltration and the formation of the SU-8-CNT nanocomposite. SU-8 infiltration is easily achievable due to the wetting of the CNTs by the SU-8. Selection of the SU-8 viscosity and spin speeds determines the SU-8 volume fraction and the smoothness of the sidewalls of the master structure. SU-8 wicks into the individual CNT structures and, depending on the spacing between the structures, may also wick in the spaces between the CNT structures. This may result in a thin film of SU-8 remaining in between closely spaced structures, and the thickness of this film can be tuned by selecting SU-8 viscosity and spin speed. The stated spin speeds result in fully infiltrated structures with heights ranging from 10 to 300 μm and with aspect ratios from 0.2 to 20. These process conditions preserve the surface texture of the CNT structures, i.e., the sidewalls and top surfaces do not bulge outward with excess SU-8.

Vacuum casting of the PDMS negative is a robust process and depends on the initial monomer to cross-linker ratio and the curing conditions. A ratio of 10:1 monomer:cross-linker is used for most castings; however, casting HAR structures ($\text{AR} > 10$) with high yield or reentrant structures remains challenging. HAR structures require a mix ratio of 8:1 due to the increased stiffness and reduced adhesion of the negative. A demolding agent, such as fluorinated silane¹⁰, may be used to further reduce the separation force required, minimizing the stress on the master microstructures during demolding and greatly increasing yield. When casting replicas, degassing is not necessary due to the prolonged baking. Degassing was found to lead to inconsistent replication, due to non-uniform evaporation of SU-8 solvent.

The main advantage of the CNT master technology is the ability to form robust master features with hierarchical textures, high aspect ratios, and sloped or curved shapes. However, this requires careful tuning of the CNT growth conditions to achieve uniform and consistent starting patterns, practical mastery of the capillary forming step, and implementation of the SU-8 infiltration and replication steps to give high-fidelity copies of the master shapes. The exact parameters may vary depending on the geometry of the desired structures, and may not be understood until many iterative trials are performed. In addition, because the amount of densification due to capillary forming depends on the density and straightness of the CNTs, prediction of the exact dimensions of the densified CNT structures will require calibration experiments to determine the densification factor. Nevertheless, our method may have important advantages if hierarchically textured and/or 3D polymer features are desired, and/or if the enhanced properties of the CNT structures (at any endpoint in the process) are desired. These enhanced properties could include the mechanical robustness, thermal or electrical conductivity of the master structures, or any like properties of the CNT features themselves.

In conclusion, we have shown a versatile process to precisely form heterogeneous CNT microstructures using capillary forming, infiltrate them, and subsequently replicate them in SU-8. In our previous work we have shown a 25-fold replication sequence is possible without any damage to the negative or fidelity reduction in the replicas⁵. Because our process is based on replica molding to cast replicas a variety of materials could be used in the future instead of SU-8 including PU, PMMA, PDMS, and even low temperature metals. Other CNT growth procedures and structures made from other nanoscale filaments (e.g., inorganic nanowires, biofilaments) could potentially serve as the framework of novel master mold architectures as well.

Disclosures

No conflicts of interest declared.

Acknowledgements

This research was supported by the Nanomanufacturing program of the National Science Foundation (CMMI-0927634). Davor Copic was supported in part by the Rackham Merit Fellowship Program at the University of Michigan. Sameh Tawfick acknowledges partial support from the Rackham Predoctoral Fellowship. Michael De Volder was supported by the Belgian Fund for Scientific Research - Flanders (FWO). Microfabrication was performed at the Lurie Nanofabrication Facility (LNF), which is a member of the National Nanotechnology Infrastructure Network; and electron microscopy was performed at the Michigan Electron Microbeam Analysis Laboratory (EMAL).

References

1. Xia, Y.N. & Whitesides, G.M. Soft lithography. *Annual Review of Materials Science*. **28**, 153-184 (1998).
2. Xia, Y., *et al.* Replica molding using polymeric materials: A practical step toward nanomanufacturing. *Advanced Materials*. **9**, 147-149 (1997).
3. Tasis, D., Tagmatarchis, N., Bianco, A., & Prato, M. Chemistry of Carbon Nanotubes. *Chemical Reviews*. **106**, 1105-1136 (2006).
4. De Volder, M., *et al.* Diverse 3D Microarchitectures Made by Capillary Forming of Carbon Nanotubes. *Advanced Materials*. **22**, 4384-4389 (2010).
5. Copic, D., Park, S.J., Tawfick, S., De Volder, M.F.L., & Hart, A.J. Fabrication of high-aspect-ratio polymer microstructures and hierarchical textures using carbon nanotube composite master molds. *Lab on a Chip*. **11**, 1831-1837 (2011).
6. De Volder, M.F.L., Park, S.J., Tawfick, S.H., Vidaud, D.O., & Hart, A.J. Fabrication and electrical integration of robust carbon nanotube micropillars by self-directed elastocapillary densification. *Journal of Micromechanics and Microengineering*. **21**, 045033 (2011).
7. Zhao, Z., *et al.* Bending of nanoscale filament assemblies by elastocapillary densification. *Physical Review E*. **82**, 041605 (2010).
8. De Volder, M.F.L., Vidaud, D.O., Meshot, E.R., Tawfick, S., & Hart, A.J. Self-similar organization of arrays of individual carbon nanotubes and carbon nanotube micropillars. *Microelectronic Engineering*. **87**, 1233-1238 (2010).
9. Nessim, G.D., *et al.* Tuning of Vertically-Aligned Carbon Nanotube Diameter and Areal Density through Catalyst Pre-Treatment. *Nano Letters*. **8**, 3587-3593 (2008).

10. Pokroy, B., Epstein, A.K., Persson-Gulda, M.C.M., & Aizenberg, J. Fabrication of Bioinspired Actuated Nanostructures with Arbitrary Geometry and Stiffness. *Advanced Materials*. **21**, 463–469 (2009).