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Room-Temperature Assembly of Directional Carbon Nanotube Strings

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Single-walled carbon nanotubes (SWNTs), due to their novel structural, electronic, mechanical, and optical properties, will find applications in many fields. Controlled assembly of remarkably flexible SWNTs[1] into various designed architectures, a key to building nanotube devices, remains a tremendous challenge. Dai et al. developed a chemical vapor deposition (CVD) approach to directed growth of suspended SWNT networks at 900 °C.[2] Progress has also been made recently in patterning SWNTs on solid surfaces.[3] We report here a new approach to the assembly of directional SWNT bridge structures at room temperature.

Our postgrowth assembly technique could, in principle, apply not only to a wide range of SWNTs in their soluble or dispersible forms,[4−8] including small diameter (0.7−0.8 nm) SWNTs,[4] covalent- and noncovalent-functionalized SWNTs,[5−8] monodispersed SWNTs with identical diameter and chirality,[9] and fullerenes@SWNTs,[10] which either cannot survive the high-temperature treatment or cannot be synthesized by current CVD method, but also to other soluble or dispersible one-dimensional nanostructures. It could enable the systematic studies of diameter- and functionalization-dependence of free-standing nanotube's physical properties without the interference of significant nanotube−substrate surface interactions. The resulting directional free-standing SWNT strings may find applications in nanoelectromechanical devices,[11] chemical and biological sensors,[12] nanotube "kinky chemistry",[13] nanoscale electronic circuits,[14] directed neuronal growth,[15] as well as transfer-printing of crossed nanotube arrays. Carbon nanotube strings can be further nano-welded to PDMS surfaces by electron beam under SEM to form robust structures.[16] It should also be possible to use focused ion beam (FIB) nanoscale-deposition to make nanoelectrodes at two ends of free-standing SWNTs.[17] An electrical breakdown technique may be used to fabricate the pure semiconducting SWNT rope by selectively removing metallic nanotubes in the rope.[18]

Micromolds with microchannel networks have been successfully employed in patterning nanowires on solid surfaces.[19] While previous experiments[19] were focused on patterning nanostructures on substrate surfaces, we found that it's possible to form suspended near-parallel SWNT strings across the microchannels on micromold itself.

The small diameter (0.7−0.8 nm) SWNTs (HiPco) (Carbon Nanotechnologies, Inc.) were sonicated in a 3:2 mixture of chloroform/chlorobenzene to give a stable, visually nonscattering solution (~3×10^{-3} mg/mL).[4] Poly(dimethylsiloxane) (PDMS) micromold was prepared according to literature[19a] and was cured at 75 °C for 2−3 h. Both ends of micromold were cut with a razor blade. Microchannels (500−700 nm in width, ~1 μm in height) were formed between PDMS micromold and native silicon substrate. A drop (0.2−1.0 μL) of freshly prepared SWNT solution was placed at the open end of microchannels, and the channels were filled via capillary action. The solution-filled microchannels were allowed to dry in the air at room temperature. The PDMS micromold was then carefully removed from the silicon substrate.

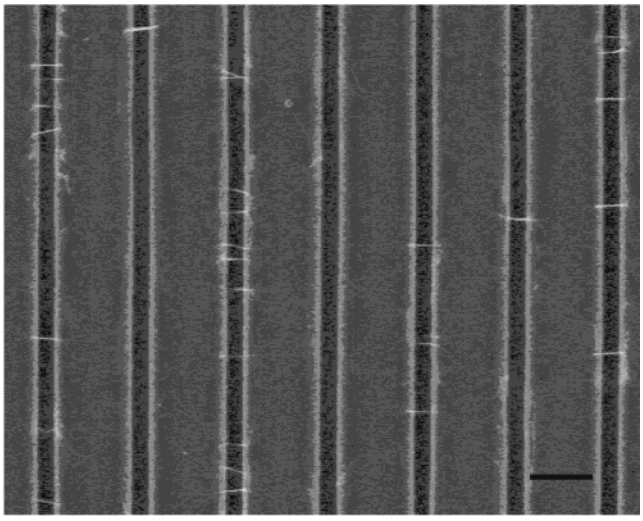

Figure 1. SEM image of suspended SWNT (HiPco) strings across the microchannels on PDMS micromold. Scale bar: 2 μm.

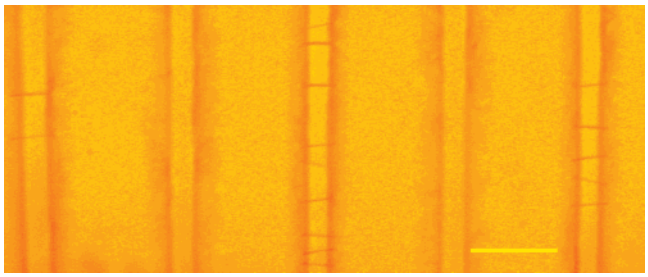

Figure 2. SEM image of suspended SWNT (laser-produced) strings across the microchannels on PDMS micromold. Scale bar: 2 μm.

Scanning electron microscopy (SEM)[20,21] showed that many near-parallel straight SWNT strings were formed across the microchannels on PDMS micromold (Figure 1). Similar results were obtained by using soluble laser-grown SWNTs[5] (diameter 1.1−1.3 nm) in a 3:2 mixture of chloroform/chlorobenzene (Figure 2). Although the detailed SWNT structures are difficult to resolve under SEM, the majority of free-standing nanotube strings are believed to be either small ropes or individual nanotubes, as indicated by previous atomic force microscopy (AFM)[4,5] studies of soluble SWNTs. We also carried out a control experiment in which a drop of blank 3:2 mixture of chloroform/chlorobenzene was placed at the open end of microchannels. No free-standing strings were found on the PDMS micromold, therefore excluding the possibility of organic solvent-induced artifacts. No detectable distortion of PDMS micromold was observed under SEM after the experiment. It's crucial to adjust the concentration of SWNTs as well as solvents to minimize the

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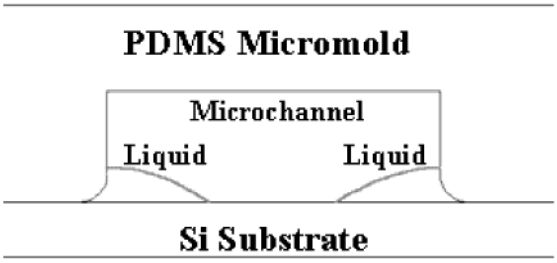

Figure 3. Schematic illustration of organic liquid inside the channel of PDMS micromold.

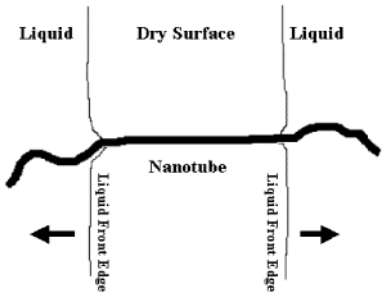

Figure 4. Schematic illustration of a SWNT between two front edges of organic liquid, and receding direction of liquid front edge.

aggregation of SWNTs on the PDMS micromold and achieve good directionality of suspended SWNTs.[21]

A possible formation mechanism of directional SWNT strings is suggested as follows: (1) Inside the microchannel, chloroform (bp 61 °C) vaporizes rapidly, and the front edge of remaining chlorobenzene liquid (bp 132 °C) recedes into the two corners of the channel (Figure 3). Yang et al. first reported this phenomenon.[19b] Upon solvent evaporation, the capillary forces are exerted by the liquid front line upon carbon nanotubes, and, as a result, some SWNTs are believed to be reoriented, stretched, and aligned perpendicular to the liquid front edge (Figure 4). (2) As the remaining chlorobenzene completely vaporizes, those SWNTs with sufficient lengths are stretched across the channel and attached to two corner surfaces of the PDMS microchannel. This also explains why the originally flexible SWNTs are as straight and tight as strings across the microchannels, which, in turn, further supported the proposed mechanism. It's likely that organic liquid occasionally penetrates into the original contact area between PDMS micromold and silicon substrate, because SWNTs with lengths considerably longer than the channel width can also be seen under SEM. When using larger microchannels with width ~4.5 μm and height ~1.6 μm, we did not find free-standing strings, which is in agreement with previous AFM observations that the average lengths of soluble nanotubes are less than 4 μm.[4,5] The exact details of the alignment mechanism are still not clear at present, and we cannot exclude other possible different alignment mechanisms.

Gerdes et al. demonstrated the ability of a single receding liquid front line to comb the SWNTs on the substrate, which also requires certain chemically functionalized surfaces to achieve the orientation of SWNTs with ~45% efficiency.[3b] The double receding liquid front lines used in the present experiments appear to significantly improve the alignment of SWNTs across the microchannels on unmodified PDMS micromold, and the orientation efficiency is estimated to be over 70% under optimized condition (Figures 1 and 2).

By carefully choosing the appropriate material and geometry of the micromold, solvents, and substrate as well as surface functionalization, it's possible to realize length-selective assembly of two-dimensional ordered, suspended SWNT strings, which could open the door to transfer-printing of crossed nanotube arrays onto chemically functionalized or electroactive surfaces.

Supporting Information Available: SEM image of suspended SWNT strings across the microchannels on PDMS micromold (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) LEO 1530 field emission scanning electron microscope (accelerating voltage: 1.00 kV). No sample coating was used in all of SEM experiments to avoid any possible artifact induced by coating.

(21) See Supporting Information.

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