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Controlled transport of latex beads through vertically aligned carbon nanofiber membranes

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Stripes of vertically aligned carbon nanofibers (VACNFs) have been used to form membranes for size selectively controlling the transport of latex beads. Fluidic structures were created in poly(dimethylsiloxane) (PDMS) and interfaced to the VACNF structures for characterization of the membrane pore size. Solutions of fluorescently labeled latex beads were introduced into the PDMS channels and characterized by fluorescence and scanning electron microscopy. Results show that the beads size selectively pass through the nanofiber barriers and the size restriction limit correlates with the interfiber spacing. The results suggest that altering VACNF array density can alter fractionation properties of the membrane. Such membranes may be useful for molecular sorting and for mimicking the properties of natural membranes. © *2002 American Institute of Physics.*

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Sophisticated forms of nanotechnology are likely to find wide spread use for biomedical applications. By either mimicking natural structures, or by interfacing biological and synthetic nanostructures, so-called bionanotechnology may enable devices for therapeutic treatment, disease diagnostics, or prosthetics. Key to the use of nanotechnology is the directed assembly of devices with nanoscale features. Such nanoscale engineering is characteristic of natural systems and will be necessary for functional use of man-made nanoscale materials as well. Vertically aligned carbon nanofibers (VACNFs) are nanostructures whose synthesis can be controlled.[1–3] VACNFs are prepared by a catalytically controlled plasma enhanced chemical vapor deposition (PECVD) process that allows for their directed assembly. The position, diameter, shape, height, orientation, and chemical composition can be reproducibly and reliably defined.[1–3] This ‘‘bottom-up’’ approach to construction can be combined with ‘‘top-down’’ fabrication techniques to realize complex microscale devices with functional nanoscale features. Here, we report the construction of dense arrays of VACNFs that serve as membranes for controlling the transport of latex beads through microfluidic channels. Such membrane devices may be useful for analytical separations of biomolecules and as functional mimics of natural membranes.

For VACNF membranes, the ‘‘pore’’ size is determined by the interfiber spacing. Both the density and area of the membrane should define the rate and the size limits of transport. This type of membrane is analogous to the artificial gel structures described by Austin and others.[4–6] In those cases, the artificial gels were constructed from micromachined silicon posts and were used for the electrophoretic separation of DNA molecules. The VACNFs described here provide the advantage of defining nanoscale structure within microscale and larger features using a single top-down fabrication step. Also, VACNF growth is an additive rather than subtractive process, so they can be grown on a wide variety of substrates, including insulating materials that are often used in fluidic applications. Furthermore, VACNFs are likely to exhibit many of the same desirable mechanical properties of related carbon materials such as multiwall carbon nanotubes (MWNTs). However unlike MWNTs, the sidewalls of VACNFs are more chemically reactive and present more options for chemical functionalization. The exquisite control of fiber placement and morphology should enable greater separation capabilities, extending to molecular scale specificity.

To prepare the membrane structures, VACNFs were grown on 3 cm×3 cm n-type (100)-oriented Si substrates. A 10-nm-thick layer of Ni–Fe (1:1) alloy on a 10-nm-thick Ti adhesion layer was deposited on the substrates. The Ni/Fe layer was used as a catalyst for growth of the VACNFs. The catalyst was patterned using contact photolithography to form 50 μm wide catalyst stripes or by deposition of the catalyst through a shadow mask consisting of a blade cut slit in Al foil resulting in irregularly shaped catalyst lines. Acety-

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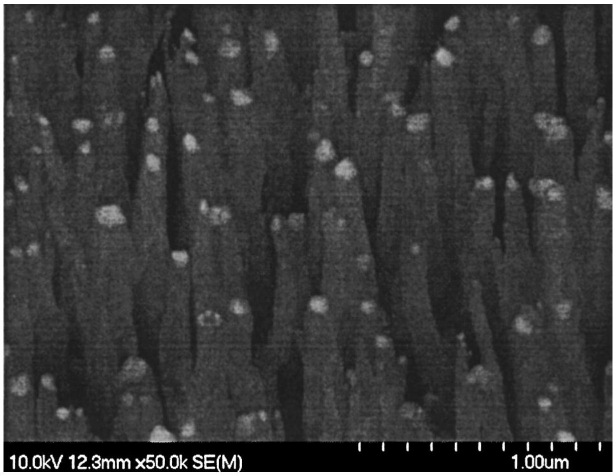

FIG. 1. Scanning electron microscopy (SEM) images of a typical VACNF forest grown from a Ni/Fe catalyst stripe.

lene (C_2H_2) as the carbon source and ammonia (NH_3) as an etchant, at gas flow rates of 65 and 80 sccm respectively, were used in the PECVD process. The dc plasma discharge was operated at 100 mA and the growth temperature was 710 °C. In all cases, the growth rate and time were selected to produce nanofibers with a height of $\sim$2.2–2.4 μm. An example of the resulting ''forest'' of nanofibers, randomly spaced within the catalyst stripe, is shown in Fig. 1. Since the same growth and catalyst conditions were used for all samples, the morphology and density of the fiber forests were similar. Further details on the growth and application of VACNFs can be found elsewhere.[1–3]

Fluid channel structures were prepared by casting poly-(dimethylsiloxane) (PDMS) (Dow Sylgard 184) onto a silicon positive relief mold.[7,8] The mold was prepared using photolithography and reactive ion etching. 50 and 100 μm wide channels, 2 μm deep and 1.5 cm long were fabricated by pouring a 10:1 mixture (elastomer:curing agent) of PDMS onto the mold, followed by a 65 °C cure for 1 h. The resulting channel structure was peeled from the mold and overlaid on the VACNF containing silicon substrate with the PDMS channel oriented perpendicular to the VACNF stripe as shown in Fig. 2. The channels were constructed to be slightly shorter than the fiber height so that the VACNFs could presumably extend into the soft PDMS lid forming a floor to ceiling barrier. The PDMS afforded relatively good sealing[7,8] to the silicon base and its transparency allowed for convenient viewing of the experiment.

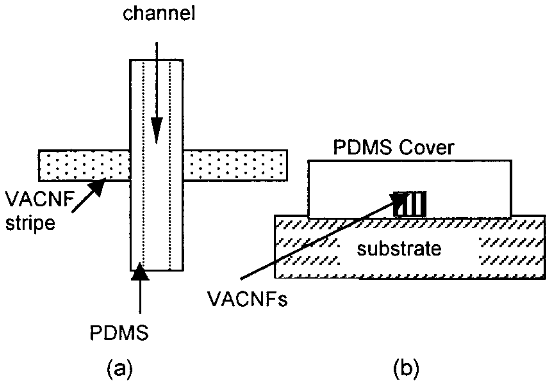

FIG. 2. (a) A top view schematic of the PDMS channel and VACNF membrane. PDMS channels were placed over the nanofiber stripes. (b) A cross-sectional view along the axis of fluid flow.

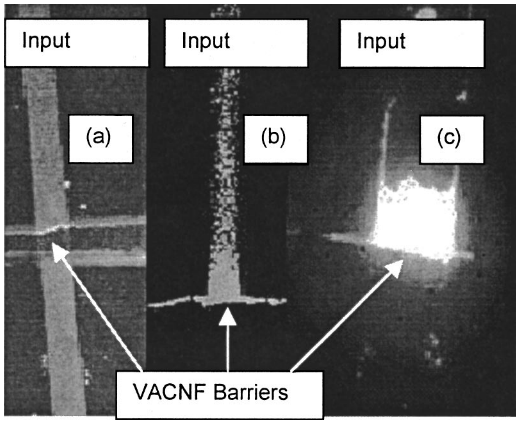

FIG. 3. Fluorescence microscope images of (a) 100 nm beads flowing in a 100 μm wide channel; (b) 500 nm beads flowing in a 100 μm wide channel; and (c) 750 nm beads flowing in a 50 μm wide channel.

The transport of fluorescently labeled latex beads was used to assess the VACNF membrane performance. Beads of various diameters, ranging from 100 to 1000 nm (Polyscience, Inc.), were diluted to 0.15% in an aqueous solution containing 1% sodium dodecyl sulfate. These solutions were introduced at one end of the open channels, and the transport of the beads was monitored using a Zeiss Axiovert 135 fluorescence microscope. Bead flow proceeded by a combination of capillary action and hydrostatic pressure. A high-resolution scanning electron microscope was used to study the morphology of the VACNFs and the distribution of latex beads after the fluidic experiment.

The membrane function of the VACNF barrier can be seen in Fig. 3. In the case of the 100 μm wide PDMS channel, beads smaller than $\sim$500 nm diffused through the fiber barrier [Fig. 3(a)], while larger beads were halted at the barrier [Fig. 3(b)]. Fluorescence on both sides of the barrier indicates that the beads traveled through the VACNFs, while fluorescence on only the input side of the barrier indicates that the beads were halted. Beads below 500 nm were able to travel through the barrier in the 100 μm wide channel, while the transport of larger beads was halted. In all experiments, beads collected at the entrance to the fiber barrier, even in the case of the smallest beads (100 nm). These observations are consistent with measurements of the interfiber spacing of $\sim 250 \, +/- 150$ nm, as determined by electron microscopy. This implies that by controlling the density of the nanofibers, the pore size of the membrane can be controlled.

Post experiment electron micrographs (Fig. 4) demonstrate the robustness of the nanofibers to mechanical and fluidic forces. Before acquiring these images, the channels were dried and the PDMS layer was removed. There was no apparent damage to the VACNFs. For experiments where beads were observed to traverse the CNF barrier, some beads were observed at the downstream end of the channels and trapped within the fiber array [Fig. 4(a)]. For cases where the VACNF barrier completely blocked transport, beads were observed to accumulate only at the entrance to the VACNF membrane [Fig. 4(b)].

These controlled transport experiments also highlight a significant practical issue concerning the construction of a

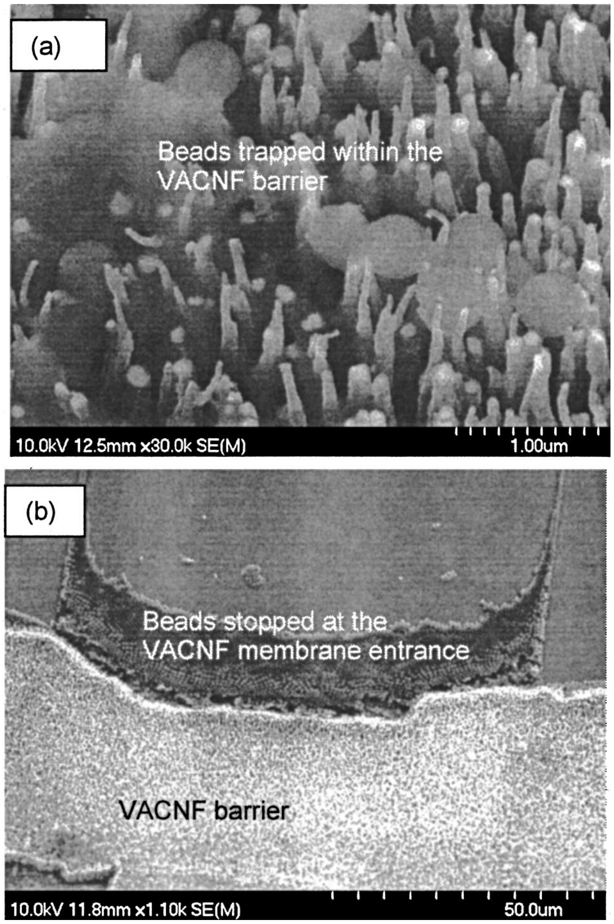

FIG. 4. Postexperiment SEM images of (a) 500 nm beads trapped within the nanofiber array and (b) 750 nm beads stopped by the nanofiber array.

sealed device containing a VACNF barrier. The PDMS sealed well along the length of the channel. However, as can be seen in Fig. 3, fluid leaked perpendicular to the channel at the edge of the barrier. This leakage was more pronounced for the fiber stripes with consistent width (Ni/Fe catalyst pattern defined with photolithography) compared to the irregularly shaped VACNF barriers (Ni/Fe catalyst pattern defined by deposition through irregularly shaped shadow mask). This is most likely related to the mechanical characteristics of PDMS. Complete penetration of the nanofibers into the PDMS outside the region of the channel may not have occurred. This could prevent a floor-to-ceiling barrier in the channel and allow beads to travel over the nanofibers. Wider channel structures can allow sagging of the PDMS across the top of the nanofibers, preventing the transport of smaller beads through this alternative path. This sagging can be on the order of a few hundred nanometers based on a Young's modulus for PDMS of $\sim 7.5 \times 10^5$ Pa.[9] Incomplete penetration of the nanofibers into the PDMS also may account for fluid leakage perpendicular to the membrane. Apparently, the PDMS detaches from the silicon surface in this region. This detachment distance, L_d, is on the order of microns and should be proportional to $(t^3h^2)^{1/4}$ where t is the thickness of PDMS and h is the height of nanofibers.[10] Therefore, a wider gap should be expected when using taller nanofibers and thicker layers of PDMS. The irregularly shaped fiber arrays apparently allowed for better contact with the silicon surface. These problems highlight the issues related to engineering on multiple length scales and must be addressed before practical implementation can be realized.

In conclusion, PDMS channels containing a stripe of VACNFs were used as initial fluidic structures to characterize the use of VACNFs as membrane structures. Fluorescently labeled latex beads size selectively traveled through the nanofiber barriers, and various widths and shapes of fiber array had different effects on the transport behavior of the beads. These results strongly suggest that VACNF arrays can serve as synthetic membranes and may be employed for controlling molecular transport.

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[1] V. I. Merkulov, D. H. Lowndes, Y. Y. Wei, G. Eres, and E. Voelkl, Appl. Phys. Lett. **76**, 3555 (2000).
[2] V. I. Merkulov, M. A. Guillorn, D. H. Lowndes, M. L. Simpson, and E. Voelkl, Appl. Phys. Lett. **79**, 1178 (2001).
[3] V. I. Merkulov, A. V. Melechko, M. A. Guillorn, D. H. Lowndes, and M. L. Simpson, Appl. Phys. Lett. **79**, 2970 (2001).
[4] W. D. Volkmuth and R. H. Austin, Nature (London) **358**, 600 (1992).
[5] D. Ertas, Phys. Rev. Lett. **80**, 1548 (1998).
[6] S. W. Turner, A. M. Perez, A. Lopez, and H. G. Craighead, J. Vac. Sci. Technol. B **16**, 3835 (1998).
[7] D. C. Duffy, J. C. McDonald, O. J. A. Schuller, and G. M. Whitesides, Anal. Chem. **70**, 4987 (1998).
[8] S. R. Quake and A. Scherer, Science **290**, 1536 (2000).
[9] D. Armani, C. Liu, and N. Aluru, 12th International conference on MEMS, MEMS 99, Orlando, FL, 1998, p. 222.
[10] J. T. Lotters, W. Olthuis, P. H. Veltink, and P. Vergeld, J. Micromech. Microeng. **6**, 52 (1996).