

TOWARD ARTIFICIAL NANOSCALE SYSTEMS: SELF-ASSEMBLED POLYMERIC TEMPLATES FOR FABRICATION OF CARBON NANOTUBE ARRAYS

Final Report

JPL Task 1026

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A. OBJECTIVES

Nanoscale technology is becoming increasingly important to NASA because it will provide a foundation for advanced spacecraft and instruments with low mass, low power requirements *and* enhanced performance and capabilities. Carbon nanotubes (CNT) hold great promise for a variety of nanoscale applications relevant to future NASA missions. In particular, regularly-spaced arrays of CNT are expected to have wide-ranging applications in the areas of sensing and communications, including high-Q, high-frequency, nano-scale oscillators; local oscillators for high-frequency receivers; nanometer-scale RF filters, signal detectors and analyzers; spectrum analyzers for mechanical vibrations; and filter media for electrophoretic separations of biomolecules (especially relevant to the thrust area of astrobiology).

In this work, we proposed to apply the principles of molecular-scale self-assembly to the creation of regular arrays of carbon nanotubes for applications in nano-scale electrical and mechanical systems. The key to this effort involves assembly on substrates of regular arrays of identically-sized nm-size particles of catalytic metals (Fe, Ni), from which can be grown regular arrays of identical CNT (and potentially nanotubes of other materials as well). The catalyst dot arrays are created using self-assembling molecular templates made from a class of molecules called block copolymers (BCP's). The objective of this work has been to demonstrate the growth of regular arrays of CNT from arrays of catalyst dots, created using self-assembling BCP films.

B. PROGRESS AND RESULTS

Block copolymers of polystyrene (PS) and polymethylmethacrylate (PMMA) were acquired from commercial sources with a variety of lengths of the two different polymer blocks. Thin films of these materials were prepared by spin-coating toluene solutions of the polymers onto Si and SiO₂/Si substrates. The thickness of the film could be controlled by varying polymer concentration or spin speed. Upon annealing for 14 - 18 hours at 165°C, these polymer films were found to self-assemble into ordered structures consisting of alternate zones of PMMA and PS. Figure 1 shows an example, an array of PMMA cylinders in a PS matrix, as imaged by AFM in phase-contrast mode (image is 1 μ m x 1 μ m). This film is a 40 nm-thick film of a BCP, consisting of 460 monomers of PS and 210 monomers of PMMA; the PMMA zones are arranged in a hexagonal pattern with a high degree of local ordering. We found that the PMMA blocks in such thin films could be readily removed by exposure of the film to UV light followed by development in acetic acid, leaving a PS film with an array of holes [1].

The next step was to use these arrays of holes as masks through which to deposit an array of dots of metal catalyst for CNT growth. Catalytic metals such as iron or molybdenum would be sputter-coated onto the array of holes, then the PS layer would be lifted off (e.g., by sonication in toluene), leaving an array of metal dots upon the substrate. Deposition of metal dots in this way proved to be somewhat problematic. It was found that the pattern of metal dots replicated the pattern of holes only for very thin polymer films, 15 nm thick or less. However, such very thin films of BCP tended to show irregularities in the size and spacing of the PMMA blocks, most likely because of strong interactions between the polymer layer and the SiO₂ surface, which is irregular on the nanometer scale [2]. We could successfully deposit metal dots only through these thin films, with their irregularities; these irregularities were then reproduced in the resulting metal dot pattern. The result is that, to date, we have been able to deposit arrays of metal dots, but those arrays show some variation in the size and separation between the various catalyst dots. Figure 2 shows a typical example, an array of dots of molybdenum deposited using a 12 nm thick PS/PMMA BCP layer as a mask (image is 1 μm x 1 μm).

This irregularity in the thin BCP layer most likely arises from differential interaction with the surface of the PMMA block vs. the PS block [2]. It has been demonstrated [2] that one way to overcome such difficulties is to coat the substrate first with a very thin "brush" layer of a random copolymer of styrene and methylmethacrylate (MMA), then spin the BCP layer on top of this brush layer. We have had some success with this approach using commercially-available random PS/PMMA copolymers, but previous work suggests that the exact ratio of styrene to MMA is crucial in achieving the best results with this technique. Ongoing work is in progress, and it may be necessary to acquire custom-synthesized random copolymers in order to perfectly neutralize the substrate surface, and so eliminate irregularities in the BCP film.

The quality of the catalyst dot arrays obtained as above was judged to be sufficient to proceed to the next step, attempting to grow arrays of CNT from these catalyst arrays. In preliminary tests, we coated SiO₂ samples with thin layers of sputter-deposited Fe whose surface-average atom density was approximately the same as that of our catalyst dot arrays. Upon heating, the Fe atoms become mobile and will tend to agglomerate into larger aggregations, or iron particles. Thus a thin layer of Fe, coated uniformly upon a surface should, upon heating, assemble itself into a randomly-distributed array of Fe particles, and thus such a layer should form a reasonable "first order" test of the behavior of our Fe catalyst dot arrays. Such a proof-of-idea test was useful because thin uniform films of Fe can be prepared easily, while the BCP-assembled dot arrays are rather more time-consuming to fabricate. In this step, we sputter-coated SiO₂ samples with Fe layers of nominal thickness 0.1 nm or less, then attempted to grow CNT on these surfaces. The samples were loaded into a tube furnace reactor, then heated to 900 - 1000°C in the presence of flowing CH₄, sometimes diluted with H₂ or Ar. Under such conditions, hydrocarbons are known to catalytically decompose upon nm-size metal particles, and the carbon so liberated forms into nanotubes. Upon exposure to these CNT production conditions, our thin-Fe-on-SiO₂ samples produced sparse arrays of straight CNT, which grew perpendicular to the SiO₂ surface. Figure 3 shows a typical result.

The quality of the nanotubes produced in these preliminary growth tests was highly encouraging, but the process appeared to have a low yield: many fewer nanotubes grew than would have been expected based on the density of Fe atoms upon the surface, which determined the number of catalytic particles that should have been present. Nevertheless, we next attempted to grow CNT arrays using the arrays of catalytic iron dots deposited using the BCP self-assembly technique discussed above. In this stage of the research, we discovered another potential

problem. The process of growing CNT from methane was observed to be highly non-reproducible; some runs gave excellent yield of nanotubes, while other runs gave few or no nanotubes. This irreproducibility of CNT growth from methane has been observed previously [3], and has been attributed to the details of the CNT growth mechanism. Specifically, when CH₄ is used as the carbon source gas for CNT, it is believed that the CNT growth occurs due to decomposition upon the catalytic particles, not of methane, but of higher hydrocarbons into which the CH₄ has been converted while traversing the hot reactor tube. Thus, CNT growth results depend strongly on such experimental parameters as flow rates, heating rates, and even the order in which gases are introduced into the reactor. To date, growth runs using our BCP-prepared catalyst dot arrays have not produced any CNT. Note that in growth experiments with these dot arrays, "witness samples," consisting of thin Fe films on SiO₂, were placed in the reactor alongside the BCP-prepared samples to verify that growth conditions were appropriate to grow CNT. In all experiments on BCP-prepared catalyst dot arrays, these witness samples also failed to grow any CNT, indicating a problem with reaction conditions, not necessarily a problem with CNT growth from the dot arrays. We are currently in the process of optimizing our growth conditions for reproducibility and CNT quality, and once this is accomplished we should be able to grow CNT arrays from our catalyst dot arrays.

C. SIGNIFICANCE OF RESULTS

We have demonstrated the use of BCP templates in fabricating arrays of dots of catalytic metals for growing arrays of CNT, and have begun to investigate the growth of CNT from these arrays. Ongoing work will address specific issues of better ordering and regularity in the self-assembled BCP materials (and resulting catalyst dot arrays), and issues of reproducibility and nanotube quality in the CNT grown from these arrays. Our initial results are encouraging, and indicate that the proposed concept (regular CNT arrays fabricated using self-assembled BCP structures) should be feasible, but clearly more research and fine-tuning is needed.

This ongoing research effort is developing the basic fabrication processes for regular arrays of carbon nanotubes for use in nanotube-based sensors, electronic components, and media for biomolecular analysis. The results of this effort will enable a variety of new sensing and instrumentation technologies, and hold great promise for a variety of nanoscale applications relevant to future NASA missions, including nanometer-scale, ultra-low mass and power sensors, electronic components, components in communications systems, and biomolecular analytical technologies of special relevance to the current thrust area of astrobiology.

The progress made in this seed effort and in complementary programs has already led to follow-on funding from NASA for a new research program aimed at using carbon nanotubes as detector elements in ultra-high sensitivity biomolecular sensors for use in extraterrestrial environments in the solar system such as Mars, Europa, and Titan ("Carbon and Silicon Nanowire Biosensors", NASA Code R, \$1.4M over 3 years, starting 10/02).

D. FINANCIAL STATUS

The total funding for this task was \$75,000, all of which has been expended.

E. PERSONNEL

In addition to the people listed on the title page, other personnel active in this effort have included Brian Hunt, Maggie E. Taylor, Daniel Choi and Roger Williams.

F. PUBLICATIONS

- [1] M. J. Bronikowski, "Regular Arrays of Carbon Nanotubes from Metal-Impregnated, Nano-Structured Block-Copolymeric Materials," NASA New Technology Report, NPO-30502. (2/02).
- [2] M. J. Bronikowski and B.D. Hunt, "Regular Arrays of Carbon Nanotubes Produced Using Templates from Nano-Structured Block-Copolymeric Materials," NASA New Technology Report, NPO-30240 (5/01).
- [3] M. J. Bronikowski et al., "Growth of Aligned Arrays of Carbon Nanotubes from Patterned Catalyst Particles," contributed talk to be presented at the AVS 49th International Symposium, Denver, CO, Nov. 3 - 8, 2002.

G. REFERENCES

- [1] T. Thurn-Albrecht et al., *Science*, 290 (2000) 2126.
- [2] P. Mansky et al., *Science*, 275 (1997) 1458.
- [3] J. Liu et al., private communication.

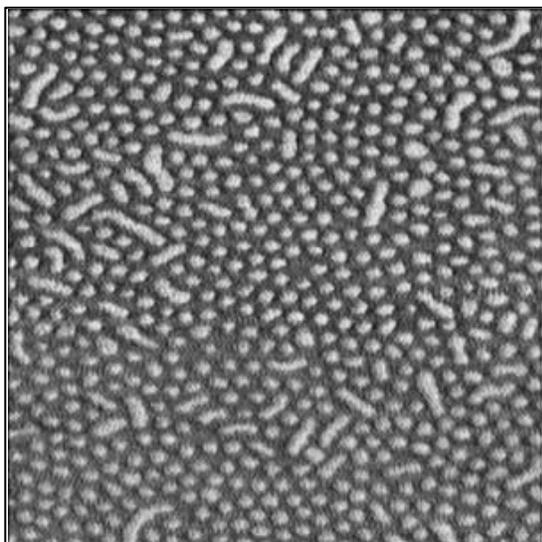


Figure 1: AFM image (phase contrast) of 40 nm annealed film of PS/PMMA, S₄₆₀MMA₂₁₀

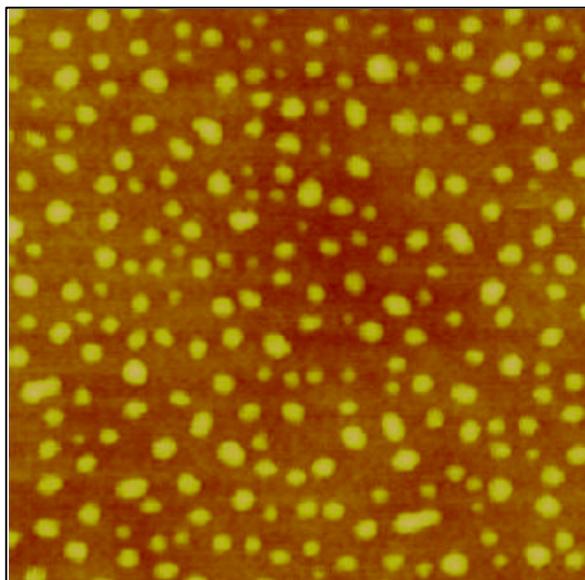


Figure 2: Molybdenum dots deposited using BCP template

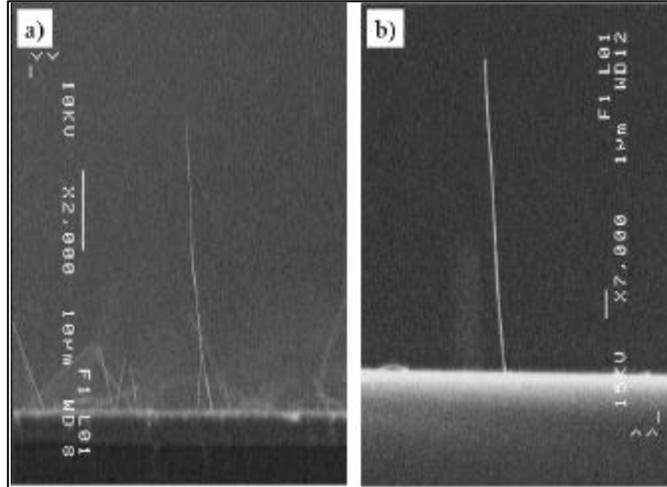


Fig. 3 a) Sparse array of CNT grown from thin Fe on SiO₂
b) Close-up of individual nanotube on this sample