

❖ Making Carbon-Nanotube Arrays Using Block Copolymers: Part 2

A nanoscale phase separation would be utilized to form regularly spaced catalytic dots.

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Some changes have been incorporated into a proposed method of manufacturing regular arrays of precisely sized, shaped, positioned, and oriented carbon nanotubes. Such arrays could be useful as mechanical resonators for signal filters and oscillators, and as electrophoretic filters for use in biochemical assays.

A prior version of the method was described in "Block Copolymers as Templates for Arrays of Carbon Nanotubes," (NPO-30240), *NASA Tech Briefs*, Vol. 27, No. 4 (April 2003), page 56. To recapitulate from that article:

As in other previously reported methods, carbon nanotubes would be formed by decomposition of carbon-containing gases over nanometer-sized catalytic metal particles that had been deposited on suitable substrates. Unlike in other previously reported methods, the catalytic metal particles would not be so randomly and densely distributed as to give rise to thick, irregular mats of nanotubes with a variety of lengths, diameters, and orientations. Instead, in order to obtain regular arrays of spaced-apart carbon nanotubes as nearly identical as possible, the catalytic metal particles would be formed in predetermined regular patterns with precise spacings. The regularity of the arrays would be ensured by the use of nanostructured templates made of block copolymers.

A block copolymer consists of two or more sections, or "blocks," each of which consists of a tailored number of monomers of a given type linked together as in a normal polymer molecule. Some combinations of monomers (for example, styrene and methylmethacrylate) yield block copolymer molecules that, under appropriate conditions, undergo a nanoscale phase separation in which they assemble themselves into repeating structures with unit-cell dimensions that typically range between 5 and 100 nm. In other words, a block copolymer can be made to acquire a regular structure on a length scale substantially larger than the indi-

vidual monomer units yet well below a macroscopic scale.

Proposed techniques for utilizing such nanostructured block copolymers as templates are generally oriented toward exploiting the differences between chemical and/or physical properties of the different materials in the adjacent nanoscale regions (for example, the hydrophilicity of the methylmethacrylate blocks and the hydrophobicity of the styrene blocks). In the version of the method described in the cited previous article, one would utilize the differences in chemical reactivities of the blocks in

order to selectively remove the blocks of PMMA, without removing the adjacent blocks of the other polymer, in order to create voids into which catalytic metals could be deposited. In the present version of the method, one would exploit differences in chemical reactivities in a different way, as described below.

In the present version (see figure), one would begin by dissolving a PS/PMMA diblock copolymer with an ionic salt of a suitable catalytic metal (e.g., FeCl_3) in a suitable amphiphilic solvent (e.g., acetone). The solution would be spin-coated onto a substrate, then heated so that the PS/PMMA block copolymer would form itself into pillars of PMMA in a PS matrix. During the heating, the Fe^{3+} and Cl^- would be expected to migrate to the PMMA regions, wherein the local dipoles in the oxygen-containing moieties would tend to attract and bind the ions. The resulting block copolymer film would contain a regular array of iron-rich and iron free regions with nanometer dimensions. The polymer would then be oxidized away by heating to a temperature of 400 °C in air, leaving a regular array of nearly identically sized and shaped iron oxide dots on the substrate. The substrate and dots would be heated in hydrogen to reduce the iron oxide dots to iron. Thereafter, carbon nanotubes would be grown on the iron dots as described above.

This work was done by Michael Bronikowski of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1)

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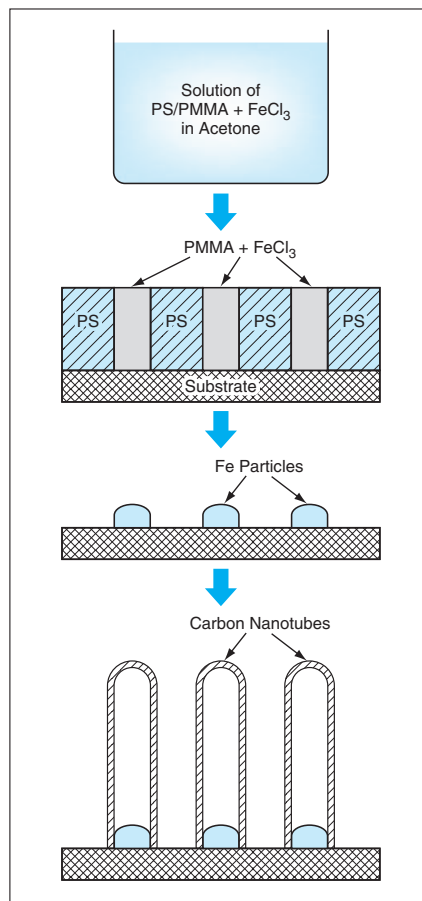
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Regularly Spaced Fe Particles would be formed at the end of a process that would exploit the tendency of Fe^+ ions to become bound in the PMMA blocks of a PS/PMMA block copolymer. The Fe particles would catalyze the growth of carbon nanotubes.