

## Block Copolymers as Templates for Arrays of Carbon Nanotubes

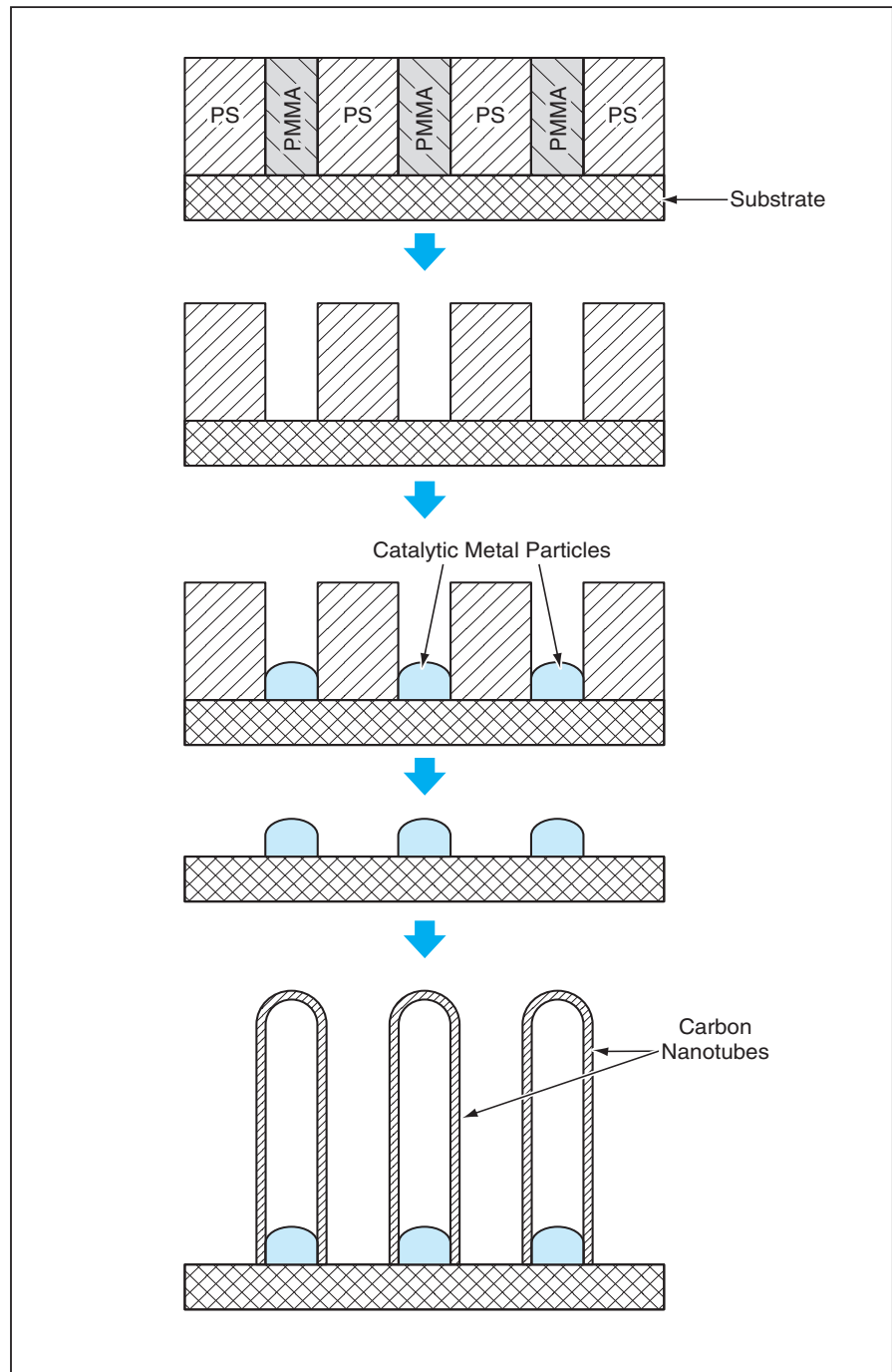
The spontaneous formation of nanostructures in block copolymers would be exploited.

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A method of manufacturing regular arrays of precisely sized, shaped, positioned, and oriented carbon nanotubes has been proposed. Arrays of carbon nanotubes could prove useful in such diverse applications as communications (especially for filtering of signals), biotechnology (for sequencing of DNA and separation of chemicals), and micro- and nanoelectronics (as field emitters and as signal transducers and processors). The method is expected to be suitable for implementation in standard semiconductor-device fabrication facilities.

As in previously reported methods, carbon nanotubes would be formed in the proposed method by decomposition of carbon-containing gases over nanometer-sized catalytic metal particles that had been deposited on suitable substrates. Unlike in 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 controlled number of monomers of a given type. Some combinations of monomers (for example, styrene and methylmethacrylate or styrene and butadiene) yield block copolymer molecules that, under appropriate conditions (for example, when heated above their glass-transition temperatures for 10 to 20 hours) 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 individual monomer units



A **Template for Deposition** of catalytic metal particles would be formed in a PS/PMMA block copolymer, then carbon nanotubes would be grown on the particles by decomposition of carbon-containing gas molecules.

yet well below a macroscopic scale. For example, when heated in an electric field, a thin film of molecules of a block copolymer consisting of sections of polystyrene (PS) connected to sections of poly(methylmethacrylate) [PMMA] undergoes a nanoscale phase separation, forming aligned, regularly-spaced cylinders of PMMA spaced apart in a matrix of PS. The size and separation of the cylinders depends on the sizes of the PS and PMMA blocks in the molecules.

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. In particular, one could utilize differences in reactivities of the blocks with respect to one or more chemical(s) in order to selectively remove the blocks of one type, without removing the adjacent blocks of the other

type, in order to create voids into which catalytic metals could be deposited.

In a typical application (see figure), one would begin by coating a substrate with a film of PS/PMMA diblock copolymer. (A typical substrate material would be silicon with a surface layer of silicon oxide.) The block copolymer film would be treated to form the desired repeating nanostructure. The nanostructured block copolymer would be exposed to ultraviolet light or to high-energy electrons, either of which would degrade the PMMA more than it would degrade the PS. The workpiece would be washed in acetic acid to remove the degraded PMMA, yielding a substrate covered with a thin film of polystyrene containing a regular array of nanometer-sized holes, into which catalytic metal could be deposited either electrochemically or from vapor. The polystyrene would be removed from around the deposited metal particles by oxidation, solvation, or etch-

ing with reactive ions. Remaining on the substrate would be a regular array of catalytic metal dots, on which a regular array of carbon nanotubes could then be grown.

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

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