# Sacrificial Post Templating Method for Block Copolymer Self-Assembly

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The morphology of thin film block copolymer (BCP) microdomains can transition between various non-bulk geometries by templating the BCP film using topographical features such as chemically-functionalized posts, as previously reported[1]. Furthermore, this templating method can be applied to more complex structures, including two-layer films[2]. After removing one block (here, the majority block of polystyrene (PS)), the resulting nanopatterns consist of both the remaining minority block (here, polydimethylsiloxane (PDMS)) and the post template (such as hydrogen silsesquioxane resist). The posts and the BCP microdomains will generally be chemically different and will have a dissimilar etch rate, and therefore could present nonuniformities in subsequent pattern-transfer and difficulties in device fabrication. Here we introduce a sacrificial-post templating method for directing BCP self-assembly in which the topographic posts are made from a removable resist. The physical post-template is removed along with the majority block, and therefore the post template is not incorporated into the final pattern. By using this method we fabricated nanoscale features in different shapes, lattices, and sizes from one BCP.

Figure 1 shows a schematic diagram of the major steps of the fabrication process. In the first step, the templates were fabricated by electron-beam-lithography exposure of poly(methyl methacrylate) (PMMA) as a negative-tone resist. The templates were chemically functionalized with a hydroxyl-terminated PS brush (1 kg/mol). Then, cylindrical-morphology PS-b-PDMS BCP with PDMS the minority block was spin cast onto the substrates with the PMMA post templates. The BCP thin film was annealed in a vapor of 5 parts toluene to 1 part heptane. An oxygen reactive ion etch (RIE) was used to remove the PS block and PMMA templates and leave the oxidized-PDMS patterns on the substrate.

Figures 2 and 3 show the experimental results of the fabrication of monolayer and bilayer nanostructures using the sacrificial-post templating method. The left and right sides of the images, with randomly oriented cylindrical PDMS, are representative of the areas where physical templates were not used. The middle regions of the images show templated BCP nanopatterns with the template removed. Insets in these figures show the locations of the PMMA posts before removal. In Figure 2, the BCP morphology transitioned from cylindrical to other morphologies due to the changes in commensurability between the post spacing and BCP period. Figure 2 c-d show nanohole arrays with a bimodal size distribution and multiplication of the templating features. Figure 3 shows bilayer mesh-shaped nanostructures. Three-dimensional self-consistent field theory simulations provided insight into the effect of post period on the morphology, shape, and size of the experimental results.

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[1] A. Tavakkoli K. G., F. Hannon, K. W. Gotrik, A. Alexander-Katz, C. A. Ross, and K. K. Berggren, Adv. Mat. **24**, 4249 (2012).

[2] A. Tavakkoli. K. G., K. W. Gotrik, A. F. Hannon, A. Alexander-Katz, C. A. Ross, and K. K. Berggren, Science **336,** 1294 (2012).

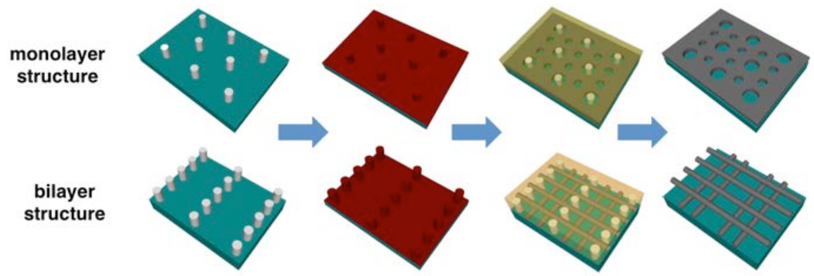


***Figure 1:*** Schematic diagram of the major steps in fabrication of monolayer (top) and bilayer (bottom) microdomain arrays using the sacrificial-post templating method. (Step 1) electron-beam lithography fabrication of arrays of posts (Step 2) functionalization of posts and substrates with a PS brush, (Step 3) spin coating and solvent annealing of the PS-*b*-PDMS BCP thin film, and (Step 4) RIE removal of the top PDMS layer with $CF_4$ then the PS matrix and PMMA posts with $O_2$.

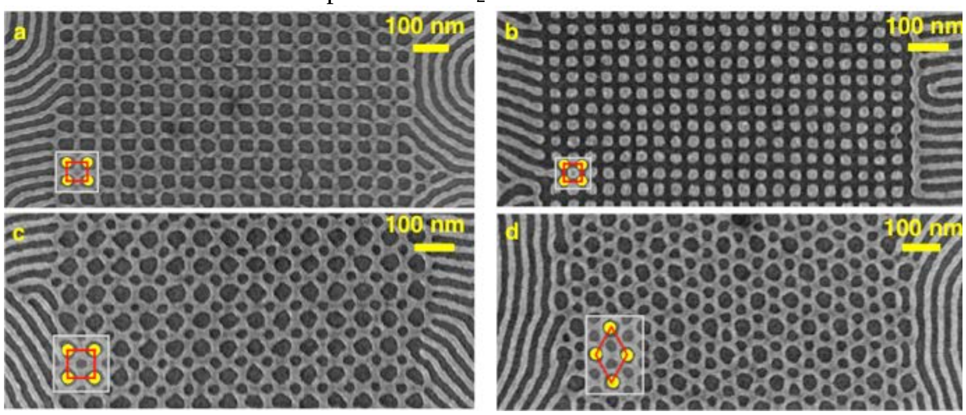


***Figure 2:*** SEMs of two-dimensional nanostructures fabricated by the sacrificial-post templating method. Shown are a (a) square array of holes, (b) square array of spheres, (c) square symmetry perforated lamella with one hole generated between each group of four posts and (d) a hexagonal symmetry perforated lamella of nanoholes with one hole generated between each group of three posts. (c) and (d) show the experimental results for bimodal size distribution.

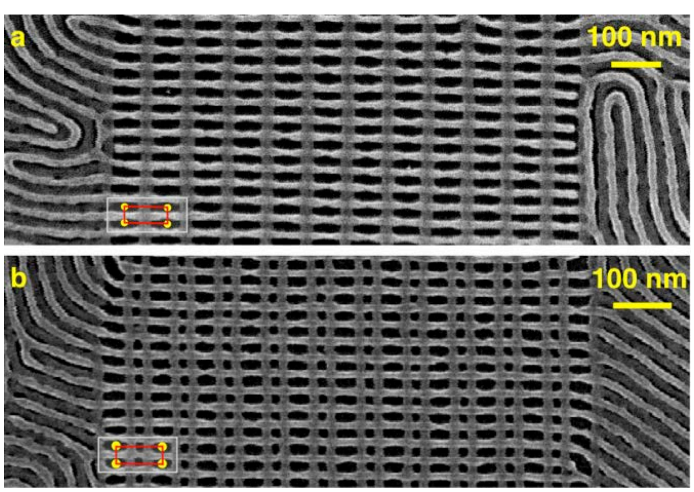


***Figure 3*****:** SEMs of mesh structures fabricated by the sacrificial-post templating method. (a) Mesh of rectangular holes, (b) mesh of bimodal rectangular holes. Light grey is the ox-PDMS and dark grey colors the substrate. Insets show the locations of negative-tone PMMA posts in yellow. Red outlines represent unit cells for the nanostructures.