Supporting Information

Large Block Copolymer Self-Assembly for Fabrication of Subwavelength Nanostructures for Applications in Optics

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The diameter of the features being subwavelength strongly affect reflectivity (close to quarter wavelength, but not prescriptively so). The smaller features do not supress the reflectivity as much as the larger features do. See Figure S1.

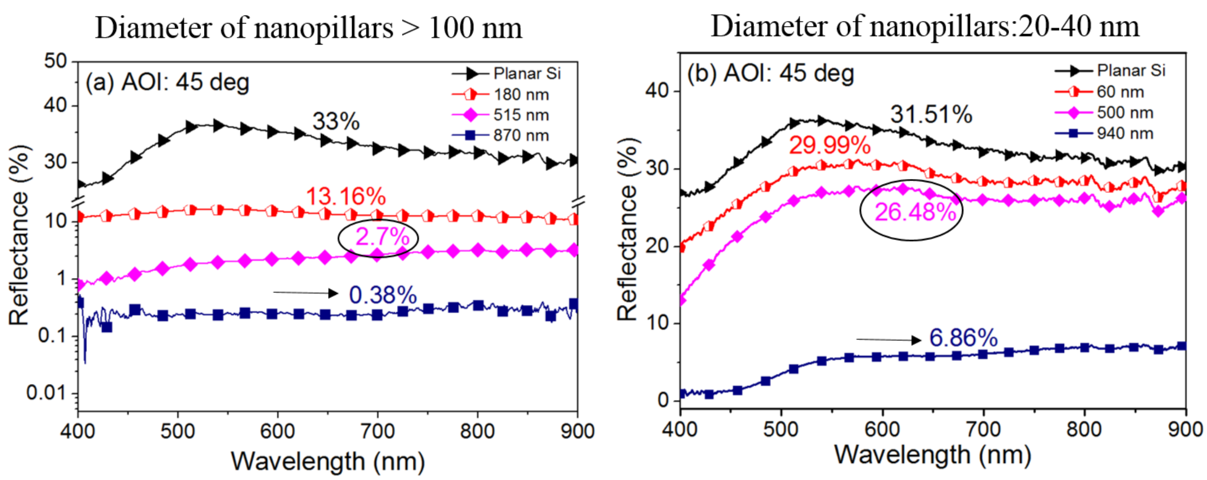


Figure S1. Comparing the reflectivity of (a) small nanopillars (diameter of 20-40 nm) with (b) large nanopillars (d>100 nm). Colors are indicative of nanopillars height. The large

dimensions nanopillars clearly supress light reflection much more effectively. The colors are indicative of nanopillars height.

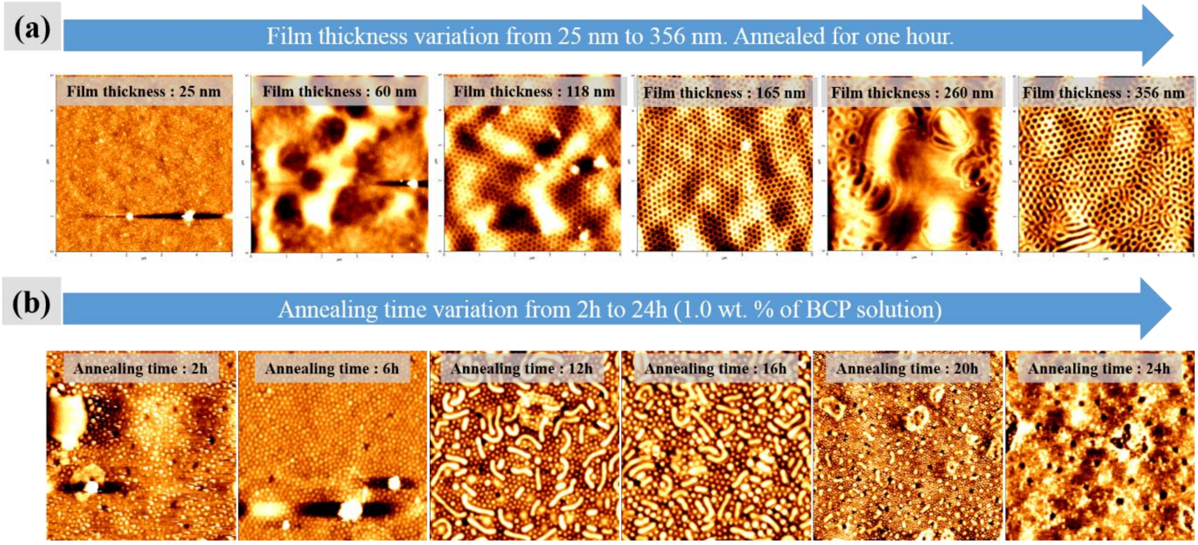


Figure S2. Film thickness and solvent annealing time variation. AFM topographic images of BCP films after solvent annealing. (a) Phase separation after an hour solvent annealing of films with a different thicknesses (b) annealing time from 2h to 24h for 1 wt. % BCP solution.

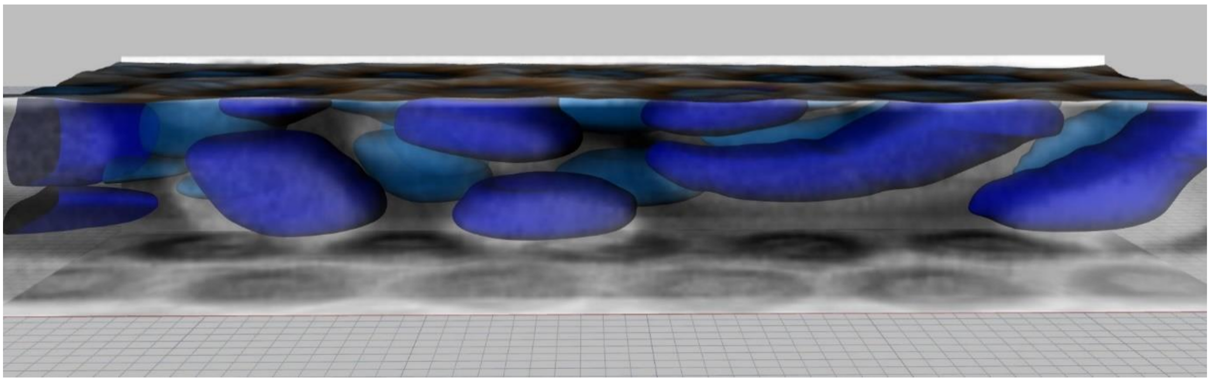


Figure S3. Visualization of the 3D modelled structure based on STEM-LAM cross section and AFM images. 3D modelled structure is constructed using the profile from STEM images and AFM images. The domains are colorised to show the layers of material. Link for the 3D video of the modelled structure: Click here

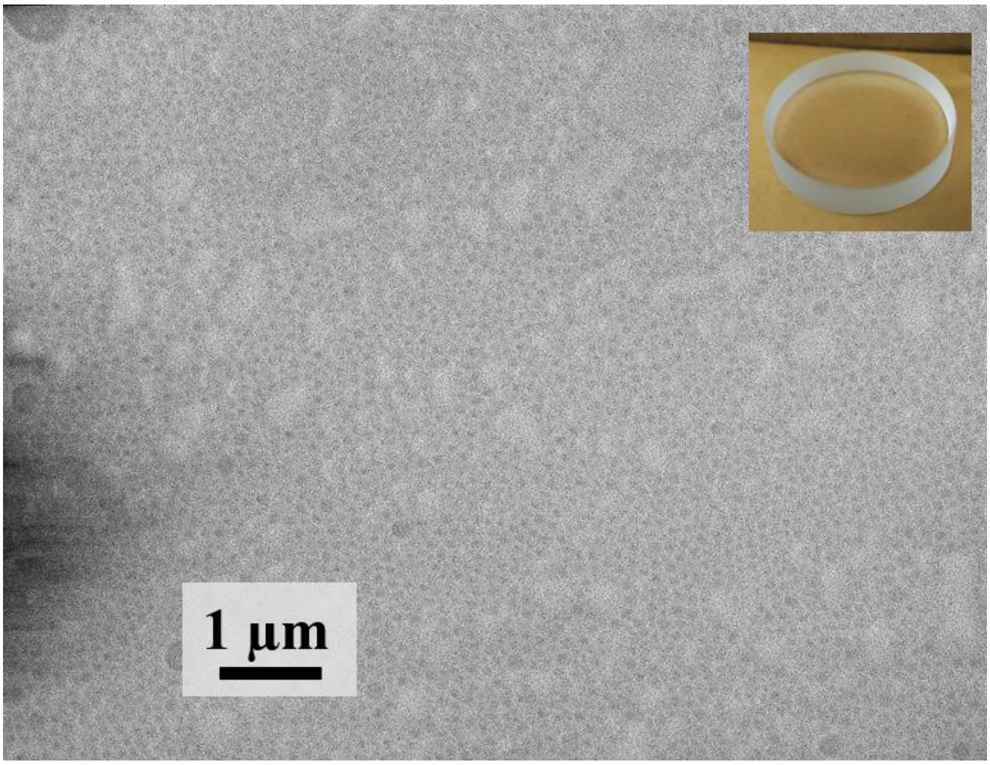


Figure S4. **Patterned BK7 convex lens.** SEM image of PS-*b*-P2VP after phase separation on BK7 convex lens. 2.0 wt. % of PS-*b*-P2VP polymer solution was spin coated on convex lens and exposed to mixed solvent of THF:CHCl3 with volume ratio of 2:1, for an hour at room temperature. Phase separated BCP thin film were stained in iodine for 6 hours to enhance the contrast difference between PS and P2VP block and image them in SEM. The inset is the optical micrograph of the lens.

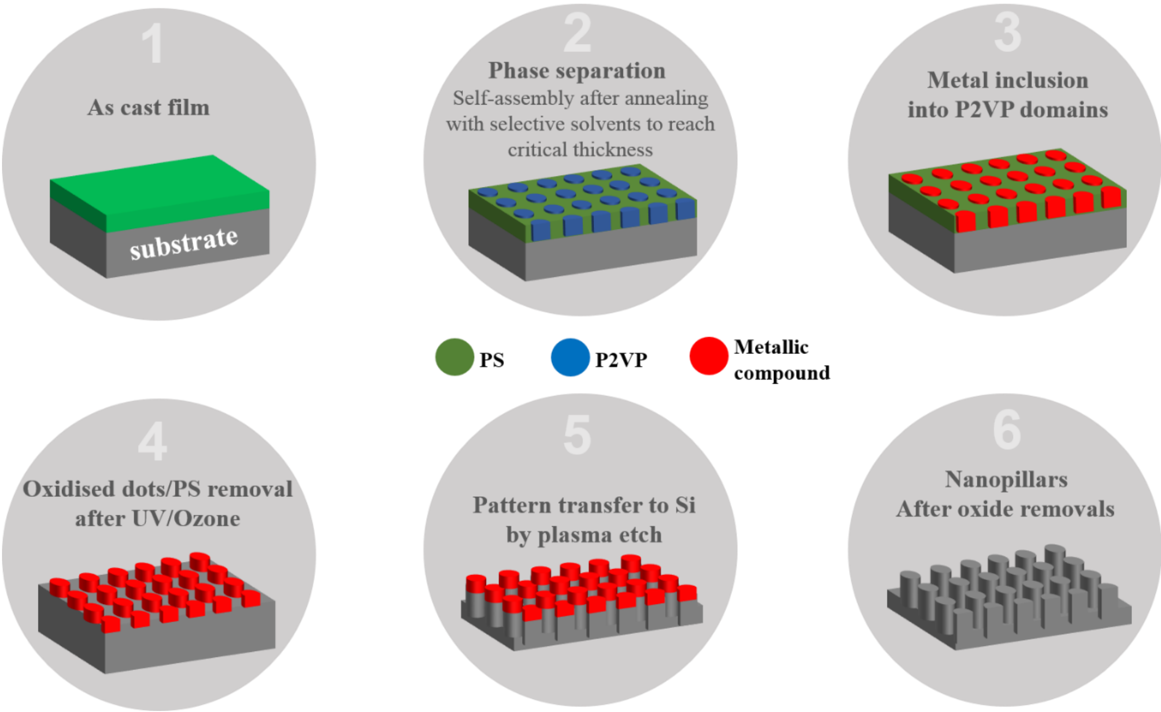


Figure S5. Schematic representation of fabrication of nanopatterned Si.

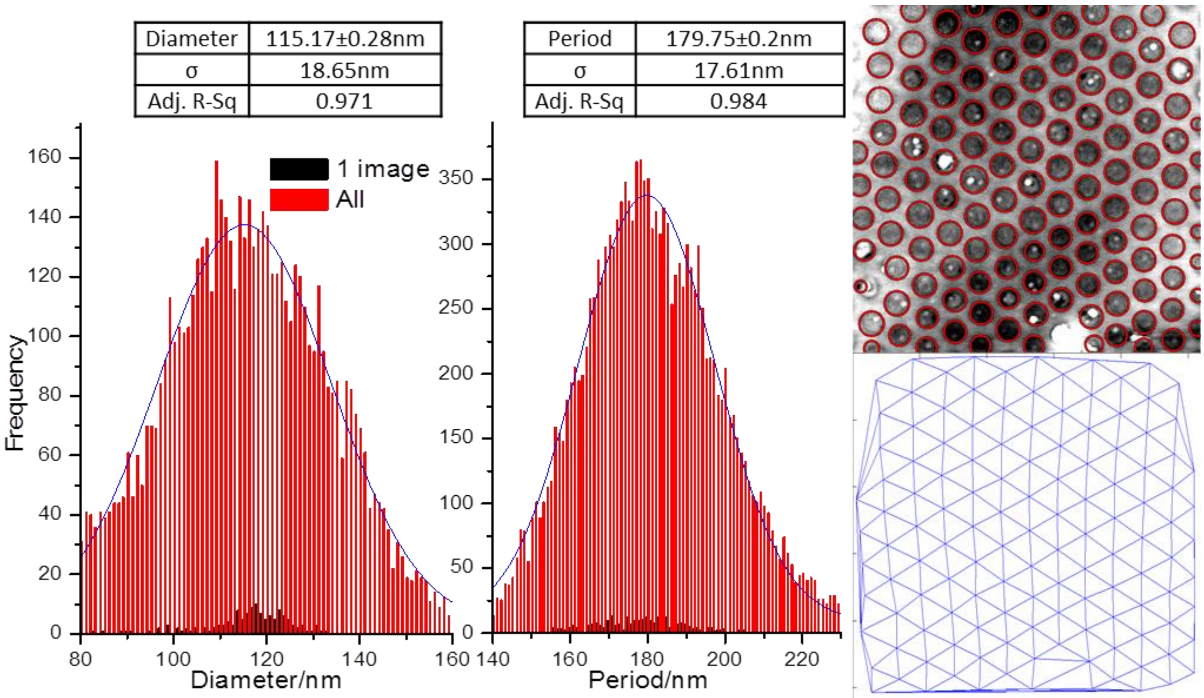


Figure S6. Size distribution for cylinder diameter (CD) (left) and period (L_0) (right) of the BCP films made on Si. Data was collected from 17 images of 10 individual samples. An example of the output detected features and Delaunay triangulation are also shown.

Methods

Film preparation. PS-*b*-P2VP (M_n = 440.0-b-353.0 kg/mol, PDI: 1.19) was purchased from Polymer Source. The polymer was dissolved in a toluene:tetrahydrofuran (THF) (80:20) mixture to yield 0.5 - 3.0 wt% solutions, and left stirring for 2 h to ensure complete dissolution. BCP films were prepared by spin coating the polymer solution onto the substrates at 4500 rpm for 30 s. Following deposition, the PS-*b*-P2VP films were exposed to mixed solvents of THF: $CHCl_3$ with volume ratio of 2:1, for an hour at room temperature. Solvent annealing was carried out in the conventional manner with two small vials containing 2 ml THF and 1 ml $CHCl_3$ placed inside a glass jar with volume of approximately 150 ml, along with the BCP sample. Phase separated BCP thin film were reconstructed by exposing the film to ethanol vapor at 40 ^{o}C for 45 minutes. A 0.8 wt. % of iron nitrate ethanolic solution was spin cast on silicon substrate as reported previously.[28] For glass and GaN substrates, and to achieve superior etch contrast a 2 wt. % of nickel nitrate ethanolic solution were deposited on the film. UV/Ozone treatment (Novascan PSD series) was used to oxidize the precursor and remove the matrix polymer.

Pattern transfer. Iron oxide nanodots fabricated on substrate surface from BCP template were used as an etch mask for pattern transfer. The silicon etch was performed using C_4F_8 (90 sccm) and SF_6 (30 sccm) gases for various duration of time with an inductively coupled plasma (ICP) and reactive ion etching (RIE) powers of 600 W and 15 W, respectively, at 2.0 Pa with a helium backside cooling pressure of 1.3 kPa to transfer the patterns into the underlying substrate. The

GaN etch was performed using CH_4 (5 sccm), H_2 (15 sccm) and Ar (25 sccm) gases for desired time with ICP and RIE powers of 500W and 45W. The glass etch was performed using Ar (45 sccm) and SF6 (5 sccm) gasses for 2 min etch time with ICP and RIE powers of 900 W and 100 W respectively. The etching process was accomplished in an OIPT Plasmalab System100 ICP180 etch tool. Figure S4 shows the schematic of the steps for the fabrication of nanopillars.

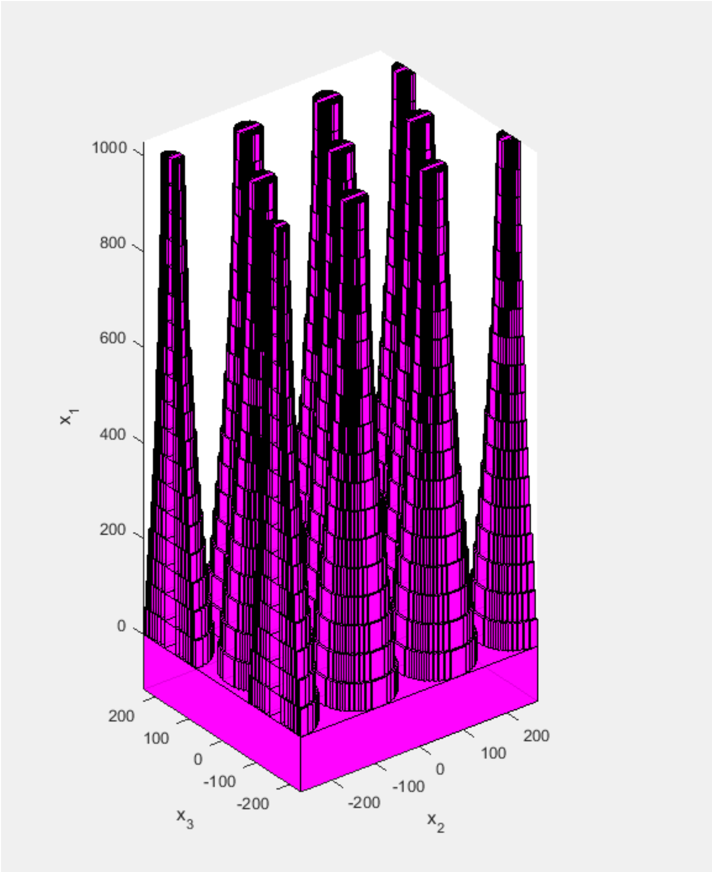
Optical analysis. Angle-resolved optical characterization was conducted using an in-house constructed cage-mounted optical reflectance/transmission spectroscopy setup. The reflectivity was obtained at variable AOI using a rotating sample stage and collection arm with constant path length. Samples were illuminated with a white Halogen bulb collimated to a beam diameter of ~ 1 - 2 mm. UV-Vis-NIR spectra of the reflected light was collected using collimation and focusing optics to two Oceanoptics spectrometers, a USB2000+ and a NIRQuest256-2.5, with optical resolutions of 1.5 nm and 9.5 nm respectively. Reference spectra were acquired using an Au mirror (ThorLabs gold mirror PF10-03-M01) at each AOI investigated prior to sample data collection under identical conditions.

Dimensional analysis. The analysis of the patterns was performed using an in-house algorithm based on the circular Hough transform and Delaunay triangulation. The extracted dimensions were fitted to a Gaussian plot to record the mean and deviation. This methodology allows us to finely measure dimensional information such as cylinder diameter and centre to centre distance (L_0) to monitor the block copolymer patterns. More information is provided in the Supplementary Information (Figure S5).

3D model. Representative 3D models were created in "Rhinoceros 5" modelling software. The profile from cross-sectional STEM images was combined with position and outlines from AFM images to form three dimensional polysurfaces. The model was then colorised to show the layers of materials.

Microscopy. Atomic Force Microscope (SPM, Park systems, XE-100) was operated in AC (tapping) mode under ambient conditions using silicon microcantilever probe tips with a force constant of 42 N/m and a scanning force of 0.11 nN. Topographic and phase images were recorded simultaneously. SEM images were obtained by a high resolution (<1 nm) Field Emission Zeiss Ultra Plus-SEM with a Gemini column operating at an accelerating voltage of 5 kV. The scanning transmission electron microscope (STEM) lamella specimen were prepared by the Zeiss Auriga-FIB (Carl Zeiss Microscopy Ltd.) with a Cobra ion column having a unique 2.5 nm resolution and were analysed by FEI Titan-TEM operating at an accelerating voltage of 200 kV.

Simulation. Optical reflectivities are simulated using the "Grating Diffraction Calculator" (GD-Calc®), an electromagnetic simulation program that computes diffraction efficiencies of optical grating structures, including biperiodic gratings. The program's capabilities include a general and flexible grating modelling facility, structure parameterization (with any number of parameters), and unrestricted control over diffraction order selection. Periodic gratings are "block-structured" (or must be defined approximately in terms of a block structured representation), meaning that the grating comprises optically homogeneous regions whose bounding surfaces are planes parallel to a set of primary coordinate planes. Moth eye-type structures are simulated as truncated cones with upper and lower diameters based on the measured structures.



S7. The simulated SiNPs