Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.


**ASSOCIATED CONTENT**

TITLE: Fabrication of Hierarchical Biomimetic Polymeric Nanostructured Surfaces

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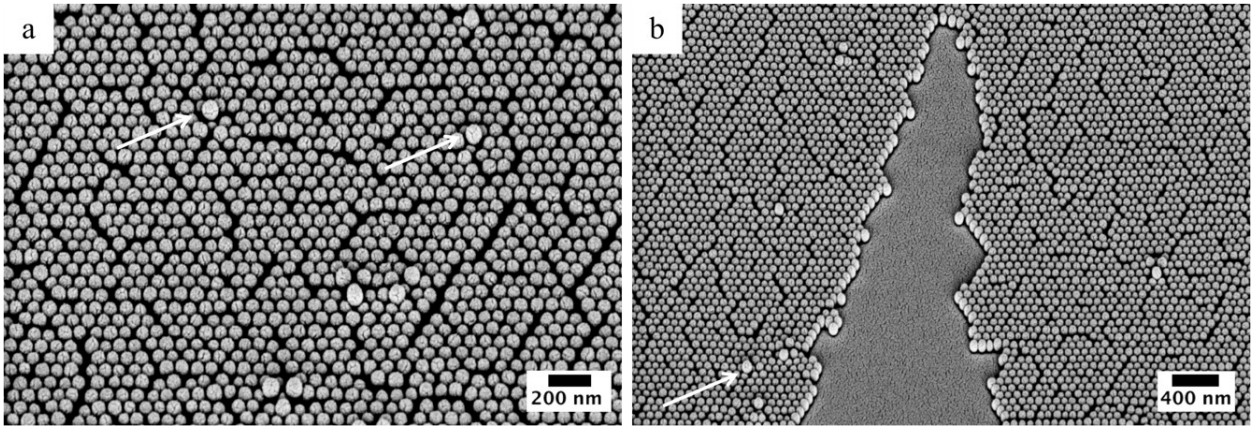
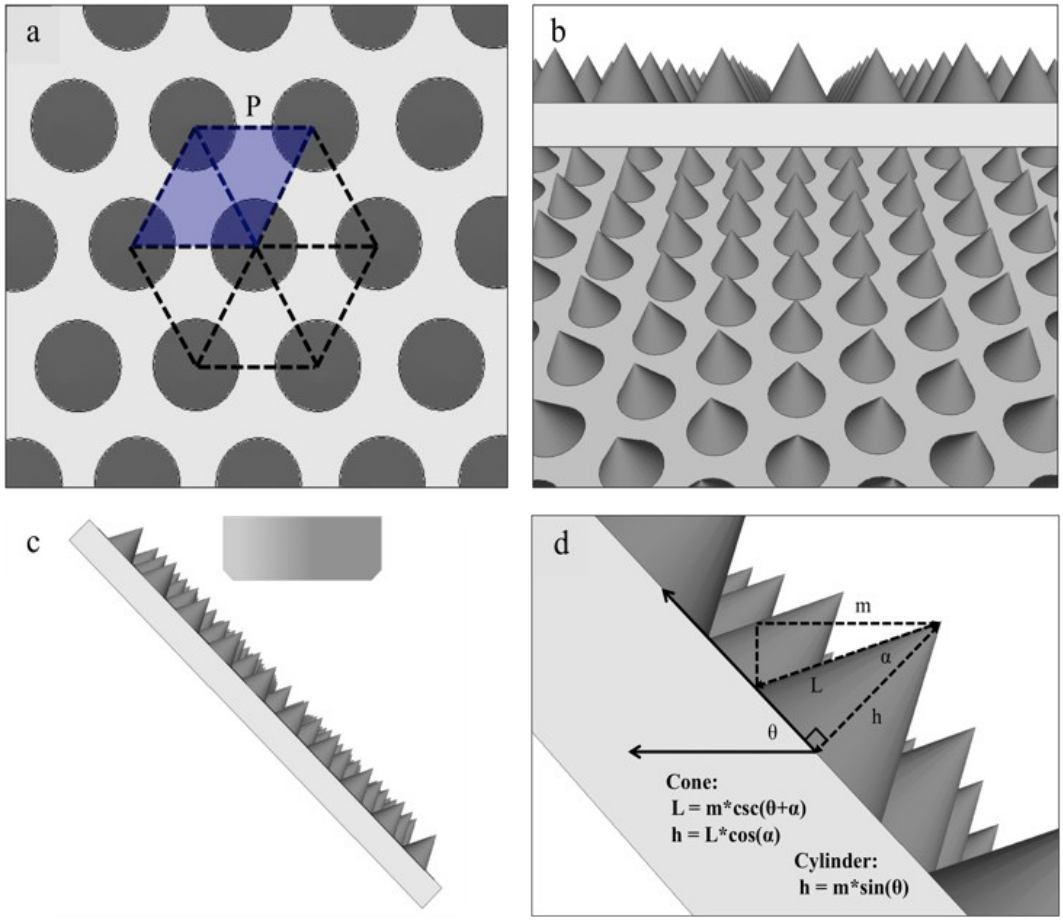
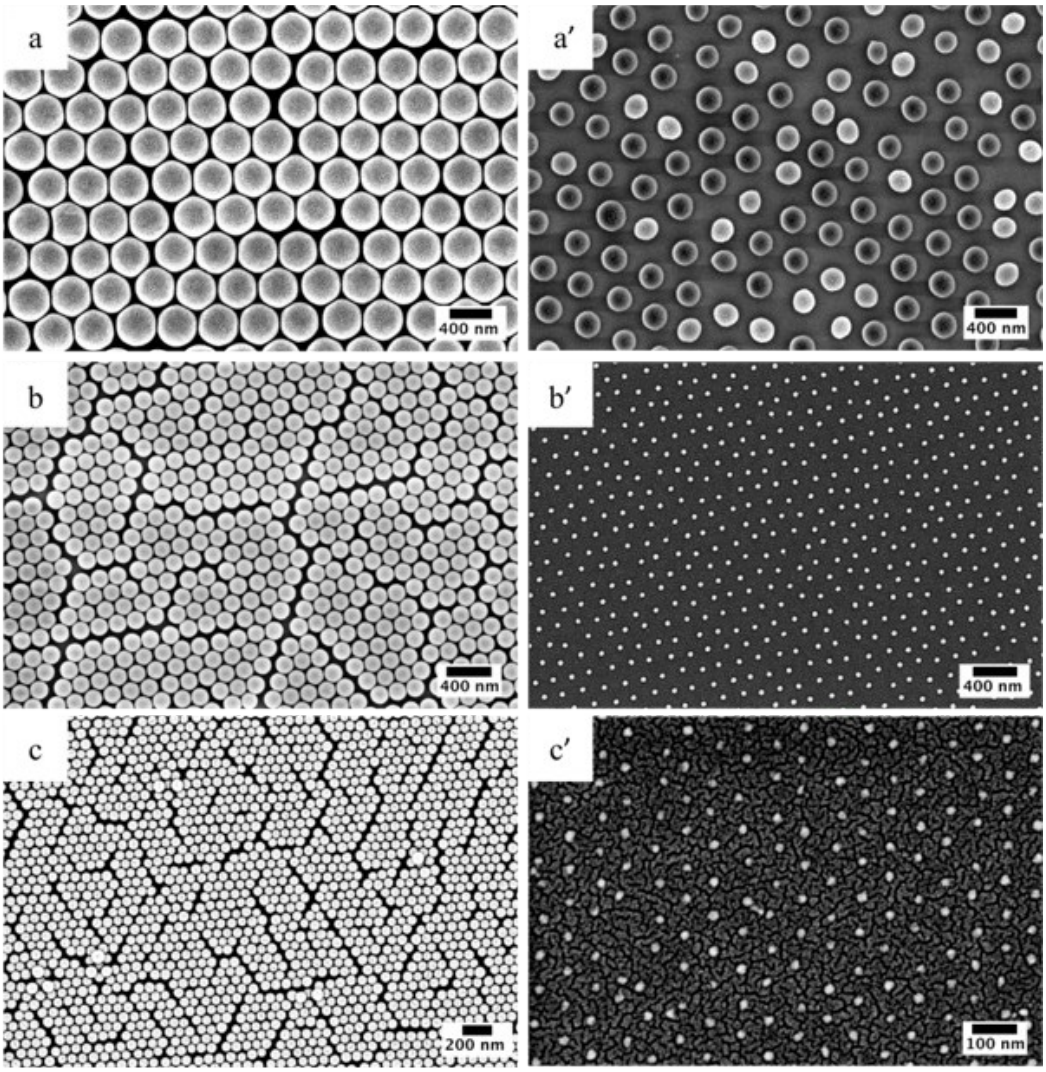



**Supplemental Figure 1: Dislocations and defects in NS monolayers**. Polydispersity Masking Defect (85nm Beads). SEM images showing larger diameter beads sitting atop the monolayer. It's likely that these beads dislocated from the film plane during the compression/assembly stage on the water surface. The phenomenon seems to be dependent on bead size or bead diameter variance/polydispersity, which tends to have an inverse relation to bead size. Smaller beads surrounding larger beads push them up out of plane during compression when SDS is added or during drying.

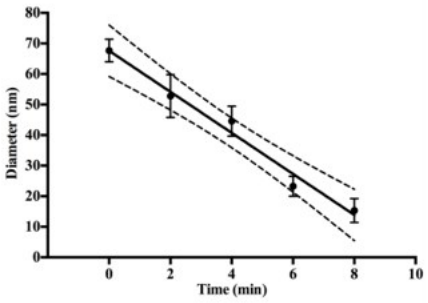



**Supplemental Figure 2: Method for spatial calculations of synthetic Biomimetic NSS**. a) Schematic representation of a face on (0° tilt) image of a conical nanoarray that illustrates the calculation of pitch or center-to-center spacing of the nanofeatures. b) schematic representation of a side view (top) and a 45° tilt view of a conical nanoarray (bottom) c) schematic representation of SEM imaging of 45° tilted sample; d) measurements and geometric descriptors: $\alpha$ - ½ vertex angle; h- height/altitude; L- lateral height/slant height; $\theta$- stage tilt; m-measured height.




**Supplemental Figure 3: Isotropic/radial shrinkage of PS NS on silicon.** a), b), and c) are etch time 0 min examples of 400, 200, and 85 nm diameter PS NS. a') shrunken NS after a 32 min PE of 400nm NS resulting in a bead diameter 183 ± 38 nm; b') shrunken NS after a 16 min PE of 200nm NS resulting in a bead diameter of 56 ± 8 nm; c') shrunken NS after an 8 min PE of 85nm NS resulting in a bead diameter of 15 ± 4 nm.

a)



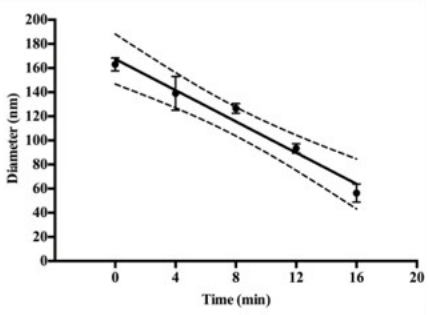

| Etch Time (min) | Mean Diameter (nm) |
|---|---|
| 0 | 67.7 ± 3.7 |
| 2 | 52.8 ± 7.0 |
| 4 | 44.6 ± 4.9 |
| 6 | 23.3 ± 3.3 |
| 8 | 15.3 ± 3.9 |

| Best Fit Equation | Mean Masking Particle Density ($cm^{-2}$) |
|---|---|
| $y = -6.7x + 67.6$ | $2.084 \times 10^{10} \pm 2.57 \times 10^{9}$ |
| $R^2 = 0.981$ | |

*Slope/Shrink Rate: (-8.4 to -5.0)

* 95% CI

b)



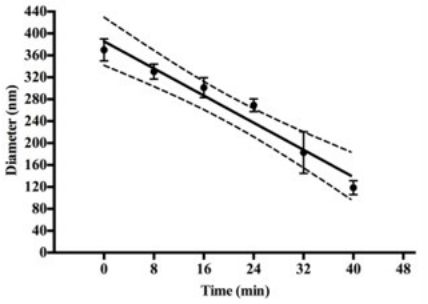

| Etch Time (min) | Mean Diameter (nm) |
|---|---|
| 0 | 163.1 ± 5.4 |
| 4 | 139.0 ± 14.0 |
| 8 | 126.5 ± 4.0 |
| 12 | 93.4 ± 3.9 |
| 16 | 56.4 ± 7.5 |

| Best Fit Equation | Mean Masking Particle Density ($cm^{-2}$) |
|---|---|
| $y = -6.5x + 167.5$ | $3.410 \times 10^{9} \pm 1.40 \times 10^{8}$ |
| $R^2 = 0.969$ | |

*Slope/Shrink Rate: (-8.6 to -4.4)

* 95% CI

c)



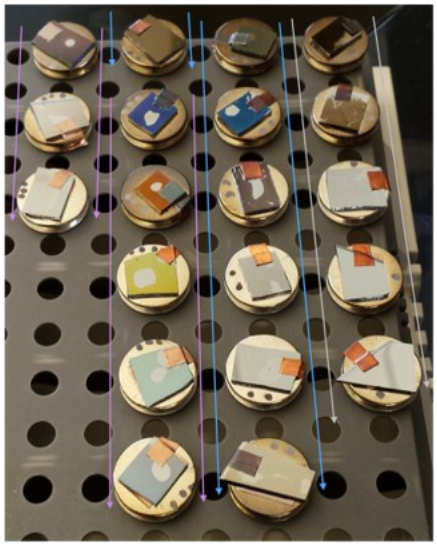

| Etch Time (min) | Mean Diameter (nm) |
|---|---|
| 0 | 370.1 ± 20.3 |
| 8 | 330.5 ± 13.8 |
| 16 | 301.2 ± 18.1 |
| 24 | 269.0 ± 11.6 |
| 32 | 182.6 ± 38.0 |
| 40 | 118.7 ± 12.7 |

| Best Fit Equation | Mean Masking Particle Density ($cm^{-2}$) |
|---|---|
| $y = -6.2x + 385.8$ | $7.573 \times 10^{8} \pm 3.81 \times 10^{7}$ |
| $R^2 = 0.958$ | |

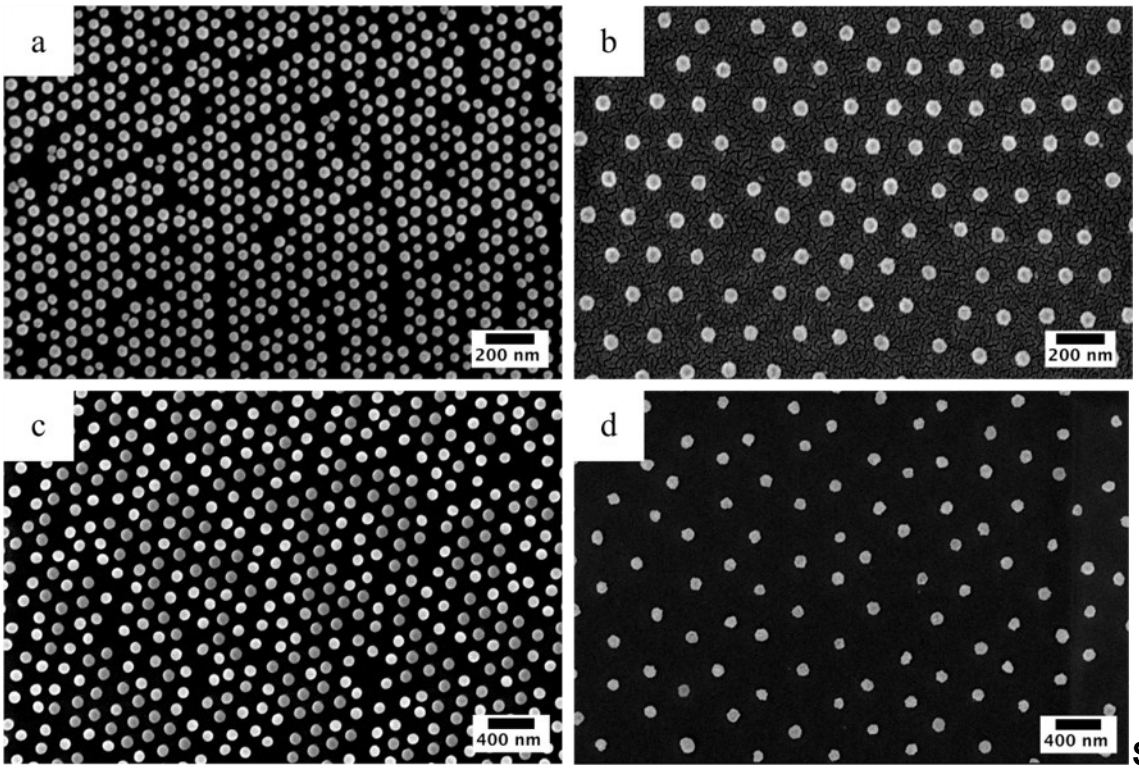
*Slope/Shrink Rate: (-8.0 to -4.4)

* 95% CI

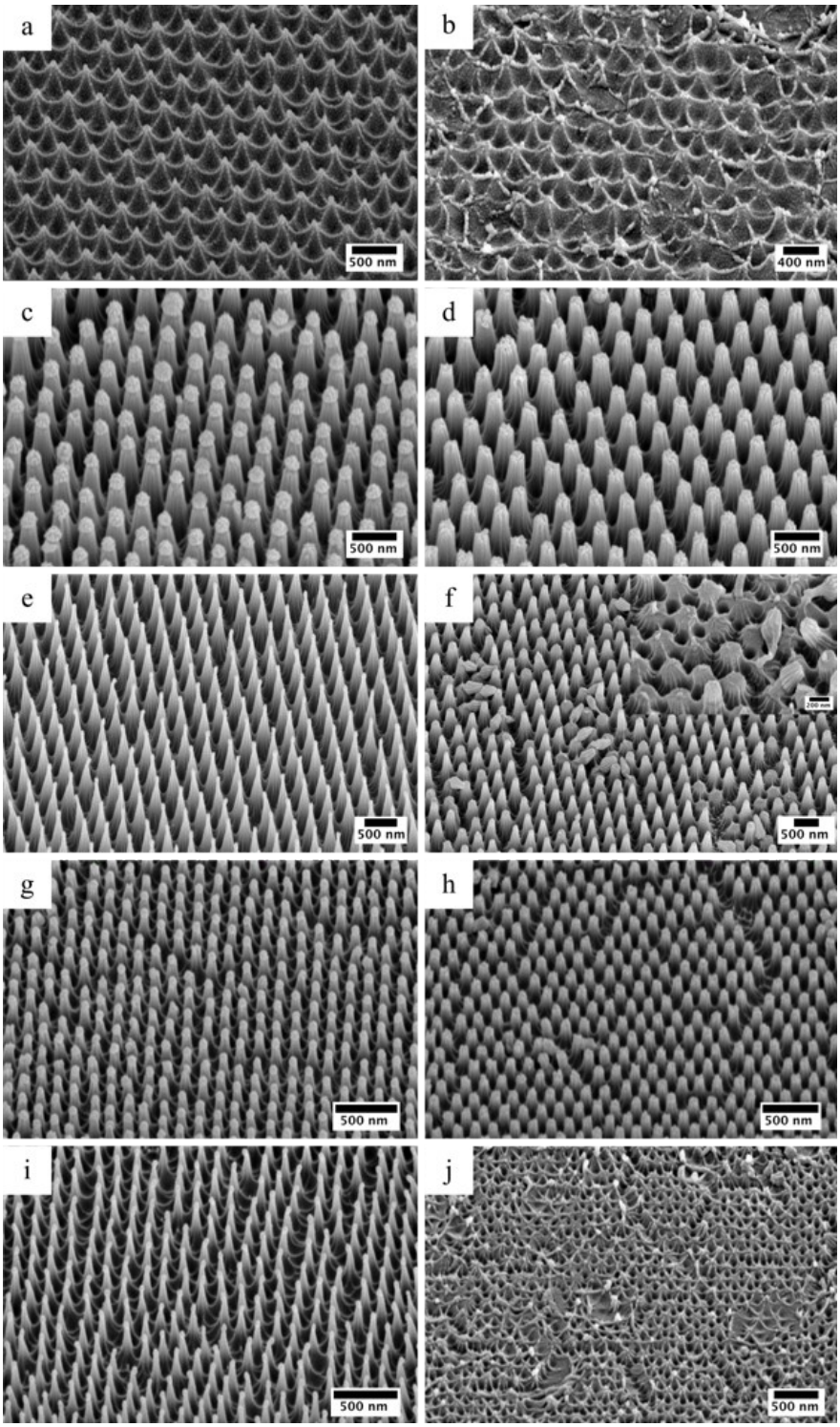
d)



**Supplemental Figure 4: Isotropic etch data for $O_2$ plasma treated PS NSs on silicon substrates.** a), b), and c) are data from PE treatment of 85 nm, 200 nm, and 400 nm NS. Dashed lines are 95% confidence intervals of slope for linear fit; d) Examples of etched substrates. Colored lines represent nominal diameters colors displayed by films and are used to label samples: violet - 400 nm, blue - 200 nm, and gray - 85 nm. As the NS shrink the color of the surfaces changes in diffuse light, particularly with 400 nm.




**Supplemental Figure 5:** Using shrink rate data on the different NS sizes we can target horizontal line intercepts such that pitch varies while particle size is conserved. a, b) are 85 nm nominal diameter at time 4 min exposure resulting in 44 $\pm$ 3 nm diameter particles and 200 nm nominal diameter at 20 min exposure resulting in 55 $\pm$ 2 nm diameter particles respectively. c, d) are 200 nm nominal diameter at 12 min exposure resulting in 93 $\pm$ 3 nm diameter particles and 400 nm nominal diameter at time 44 min exposure resulting in 113 $\pm$ 6 nm diameter particles.




**Supplemental Figure 6. Sonication Induced Damage to synthetic polymeric NSS.** Left column pre-sonication. Right column post-sonication, 10 minute treatment. (a, b) 10 min isotropic PE/400 nm NS mask on PET; (c, d) 60s RIE/400 nm NS mask on PET; (e, f) 90s RIE/400 nm NS mask on PET;(g, h) 30s RIE/200 nm NS mask on PET; (i, j) 45s RIE; 200 nm NS mask on PET.