Supporting Information

Confined Etching within 2D and 3D Colloidal Crystals for Tunable Nanostructured Templates: Local Environment Matters

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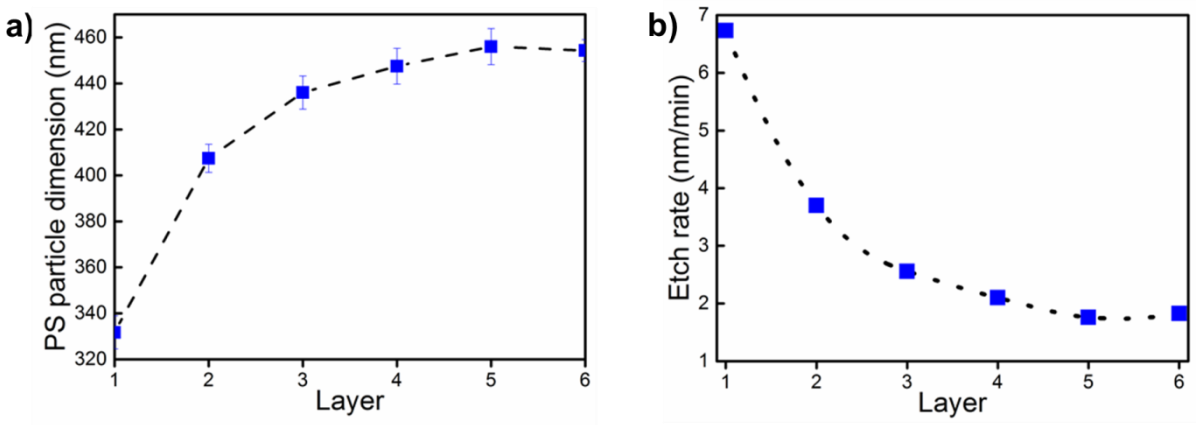

Figure S1. Local etch rate within 3D crystals. a) PS particle size (edge-to-edge distance) evolution after 25 minute etching multilayered 3D PS crystals on Si substrates as a function of the particle location (layer 1 = top layer – crystal-air interface, layer 2 = layer below the top layer etc.). The error bars correspond to the standard deviation of more than 20 measurements. The black dotted line is a guide for the eye. b) Approximate etch rate as a function of layer, calculated from the data shown in a. The dotted line is a guide for the eye. Both graphs correspond to Figure 5b in the main text.

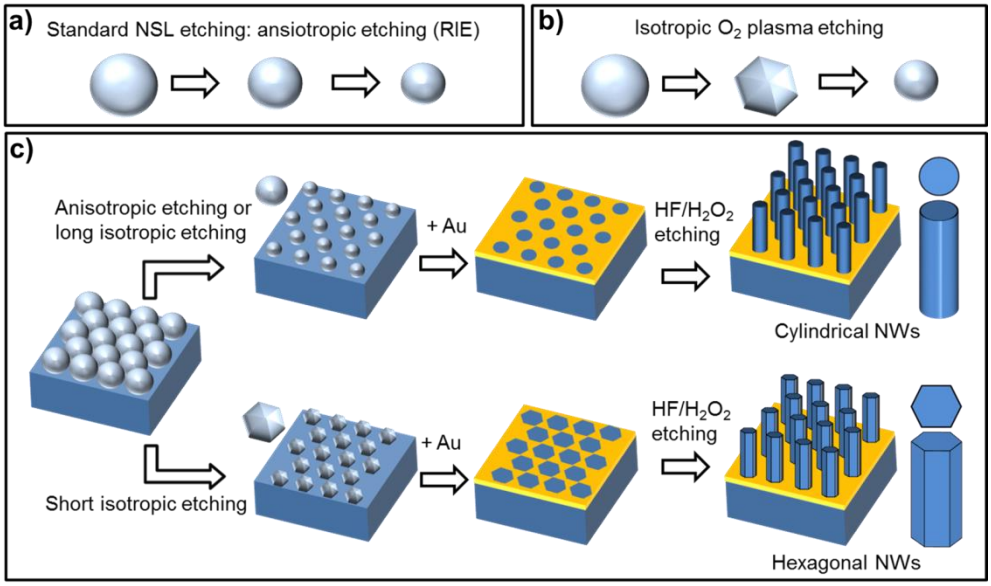

Figure S2. Strategy to generate Si nanowires with tunable morphologies using isotropic O_2 etching during NSL and MACE. a) Schematic showing the effect of anisotropic etching based on reactive ion etching (RIE) as it is done in conventional NSL: the original circular cross-section is preserved. b) Schematic showing the effect of isotropic O_2 plasma etching done in this work: the initially circular cross-section of the PS spheres becomes hexagonal after a short etching step, and eventually becomes circular after longer etch. c) Schematic of the combined NSL and MACE process. A hexagonal close-packed monolayer of PS spheres is generated via spin-coating on Si. (Top) Anisotropic etching or long isotropic etching steps produce loosely packed PS particles with spherical cross-sections. Sputtering of ZnO:Al/Au followed by lift off yields a hexagonal array of circular gold nanoholes. Finally MACE in HF/H_2O_2 produces cylindrical Si nanowire arrays. (Bottom) Short isotropic O_2 plasma etching leads to loosely packed PS particles with hexagonal cross-sections, resulting in Si nanowires with a hexagonal morphology after NSL and MACE.

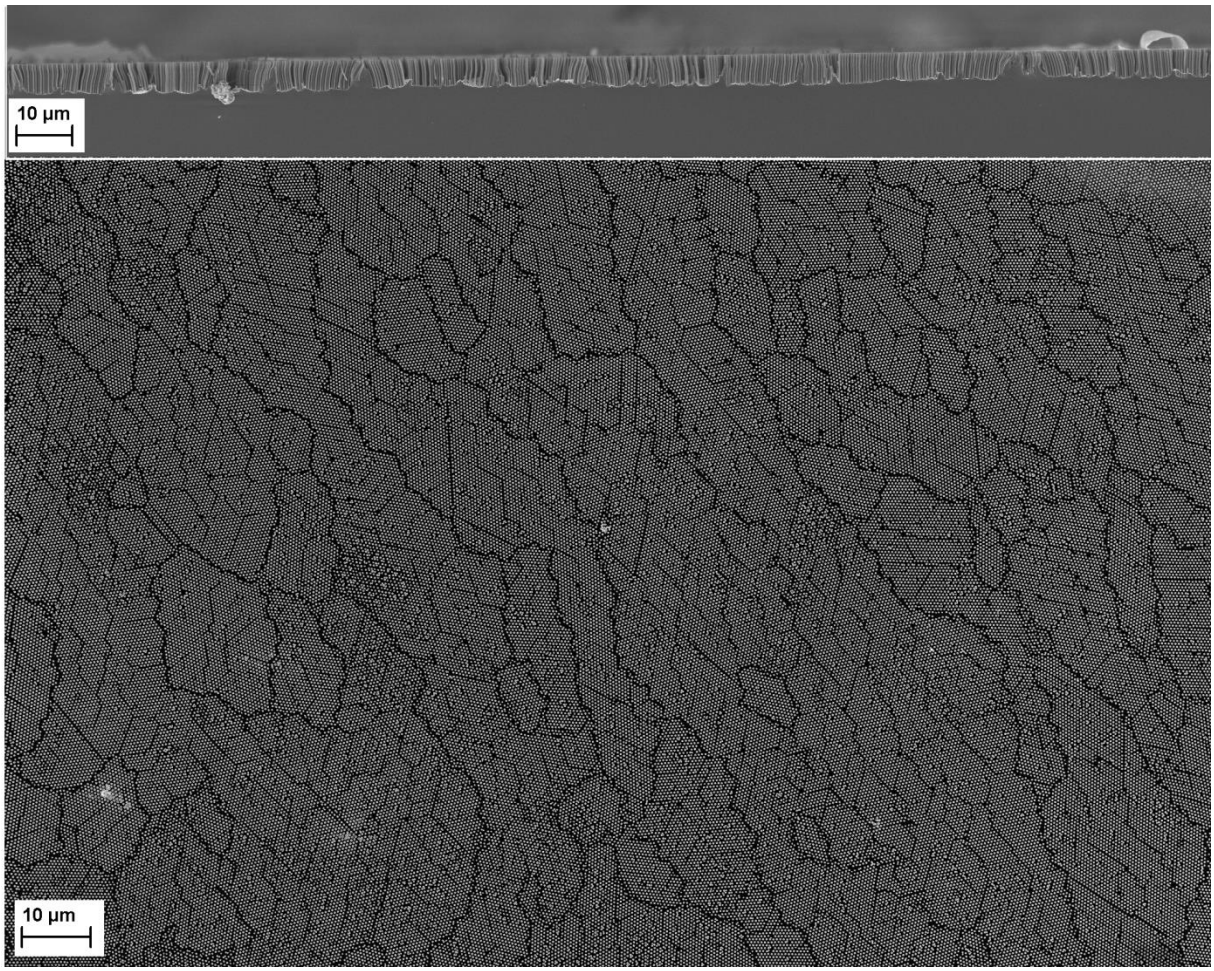

Figure S3. Large - scale array of silicon nanowires obtained with MACE.

$$MF = \frac{(d-h)}{d} \times \frac{1}{0.1340} \times 100$$

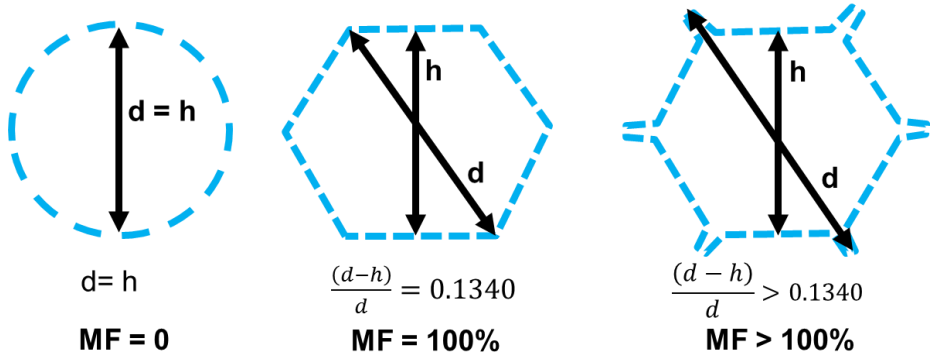

Figure S4. Morpholgy factor (MF). Influence of cross-section shape on MF. From left to right: a circle, d=h; a perfect hexagon, d/h=2/√3; an elongated hexagon, d/h > 2/√3.

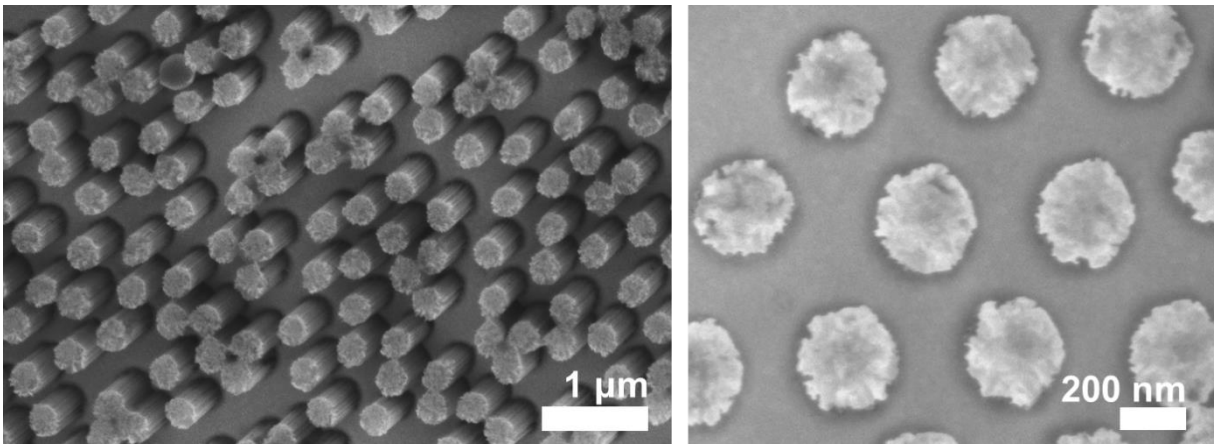

Figure S5. **Cylindrical Si nanowires.** SEM images of Si nanowires produced using 500 nm PS sphere monolayer etched in O_2 plasma during 30 minutes and 120s MACE.

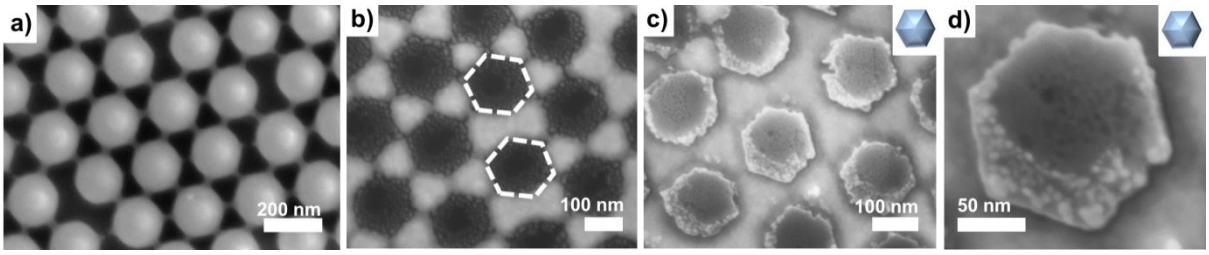

Figure S6. **Nanostructures produced using 200 nm PS spheres**. (a-d) SEM images. a) PS sphere monolayer etched 15 minutes in O_2 plasma. (b) Resulting Au hexagonally shaped nanohole array on Si after ZnO/Au deposition. c-d) Hexagonal Si nanowires produced by performing MACE on the gold mask shown in b).