Self-Assembly Schemes for Fabrication of Inverse Opals

Standard Operating Procedures

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1.SOP Objective

The standard operating procedure for: the self of assembly of spherical micron sized particles, the inversion of assembled particles into porous material with sub-micron struts, and the creation of templates for self-assembly using a positive resist, oil immersion technique on the Nanoscribe.

The first two techniques are beneficial to anyone in the community looking to work with the self-assembly of microparticles while the third is highly applicable in a wide range of applications for Nanoscribe users. These include creation of masks, lift-off-layers, and a wide variety of complicated 3D templates.

2.SOP Description

2.1 Self assembly of micron sized spheres

Self-assembly has shown to be an effective method of producing ordered colloidal structures which can grow to the mm scale with sufficient particles and time. This method is comparably cost effective as opposed to direct laser writing or other techniques that produce 3D periodic microscale features. While creating self-assembled structures, the particle-particle and particle-surface interactions greatly affect the order of the produced structure. For this reason, this project itself to systems with minimal particle-substrate interactions. Highly monodisperse 4 um PMMA spherical particles (analytical standard) were assembled in PDMS wells on either a silicon substrate or a glass coverslip. In order to quantify the order of one assembly compared to another, a radial distribution function (RDF) is used. This method provides information about the periodicity and packing density. This method is shown for the monolayered assemblies but can be applied to cross-sections or any planar surface of the assembled structure. This project uses this method as a quantitative metric to analyze the order of the assembled structure.

2.1.1 Creation of self-assembled sphere layers

1.) Prepare the well. For this project, 4mm wells are cut from PDMS (using a biopsy punch) and secured to the substrate after plasma treatment for ~1 minute (air/nitrogen). The wells are then left in ambient air for 2+ hours to allow the surface to passivate.
2.) Dilute the bulk particle solution (10% concentration) in MilliQ water. This step is done only for assembly of monolayers. It allows for ease of measurement of solution volume into the well. This project uses a 50:1 MilliQ water to bulk particle solution (0.2% concentration).
3.) Pipet the particle solution into the well. For multilayered assembly, 5 μL bulk solution (10% concentration) was used; for monolayered assembly 15μL 50:1 solution (0.2% concentration) was used.
4.) Top off the well with MilliQ water. This allows for the particles to sediment at the bottom of the well evenly before the evaporation of the fluid.
5.) (optional) To improve the order of the assembly, prevent evaporation of the fluid and shake the wells on a shaker table at ~100rpm. Evaporation is prevented by

placing the well in a petri dish with external water then covering it with parafilm (increasing the effect humidity of the environment).

6.) (optional) To improve in, use a substrate with a template (such as a trench) which will act as a site for particle alignment
7.) For use in sol-gel process, dry the particles out slowly. This is generally done in ambient air, partially covered for 12-24 hours.

2.1.2 Quantifying level of order using Radial Distribution Function (RDF)

RDF calculates the probability of a particle existing at a particular radius from each other particle. This is commonly done for atomic structure analysis in material science/chemistry. This processing is done in ImageJ and uses the RDF macro plugin[1].In order to do this process, the application and plug-in file must be downloaded. To analyze the order of assembly, two metrics are considered: the first peak and the full width at half max (FWHM). The location of the first peak indicates the nearest neighbor distance which gives the periodicity (this should be the diameter of the particles) The FWHM of the first peak indicates the distribution of the packing, with a smaller FWHM indicating a more closed packed structure. To ensure that these metrics are consistent across different sample images, the integration under the first peak (this indicates how many particles are surrounding a single particle) should be approximately equation to each other across different images.

1.) Open image in ImageJ and convert it to 8-bit through Image->Type->8-bit.

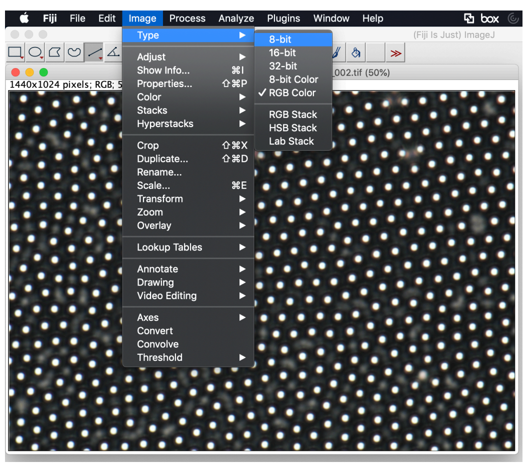

Figure 1: Converting image into an 8-bit through ImageJ

2.) Adjust the threshold histogram so that only the peaks remain. Go through Image-> Adjust->Threshold. Make sure to select to apply the threshold.

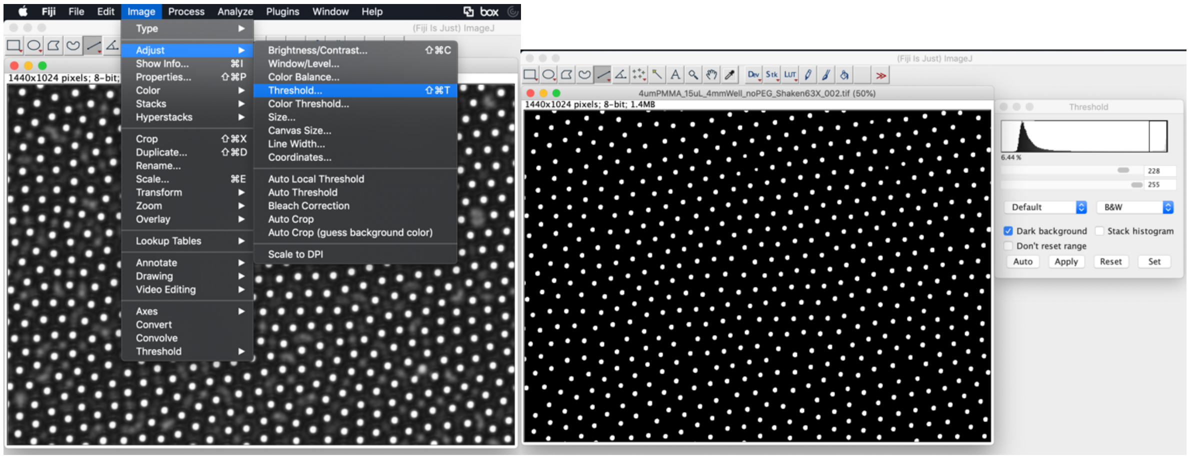

Figure 2: Thresholding an image to get binary data in ImageJ

3.) Menu Edit->Invert. This step is done in accordance with the plug-in

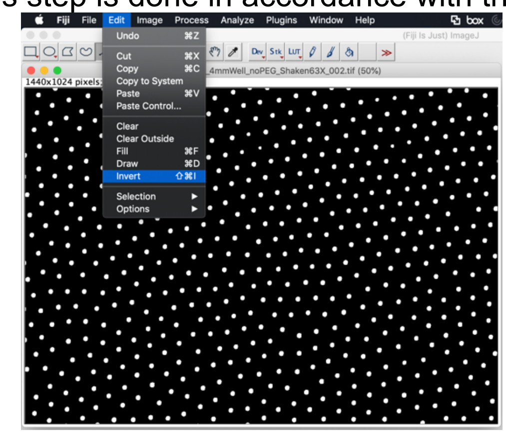

Figure 3: Inverting the binary image in ImageJ

4.) Go through Process->Find Maxima and check the boxes for Strict, Exclude Edge Maxima, Light Background, and Preview Point Selection. This step is done to verify that the correct points are being found.

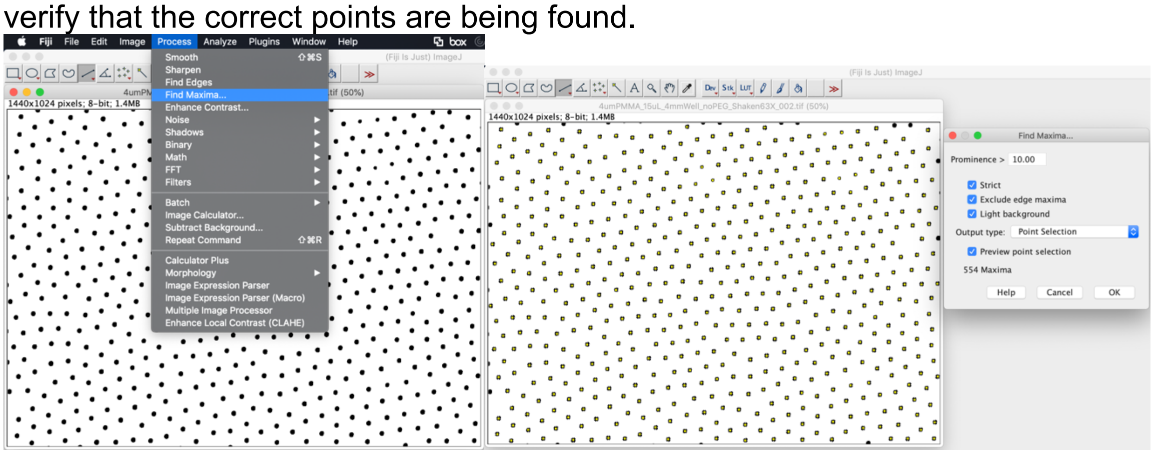

Figure 4: Finding points within the binary data for calculation of RDF in ImageJ

5.) Go through Plugins->Macros->Install… and selection the file downloaded

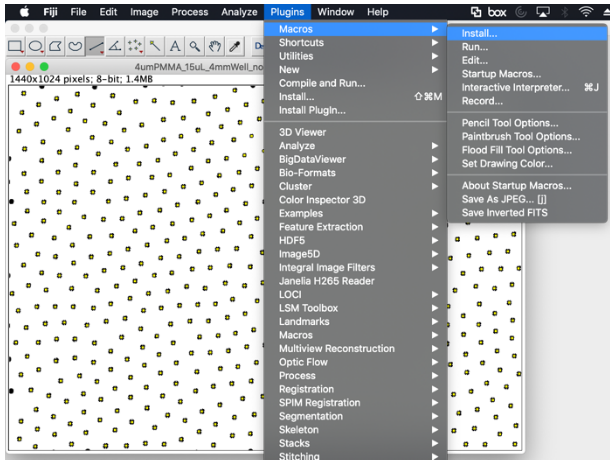

Figure 5: Installing a macro function for RDF generation

6.) Go through Plugins->Macros->Radial Distribution Function to run the program. The program will output a plot of the RDF and a list of points which can be saved as a text file. Note that the x-axis will be output in pixels and need be converted into real units based on the scale of the image.

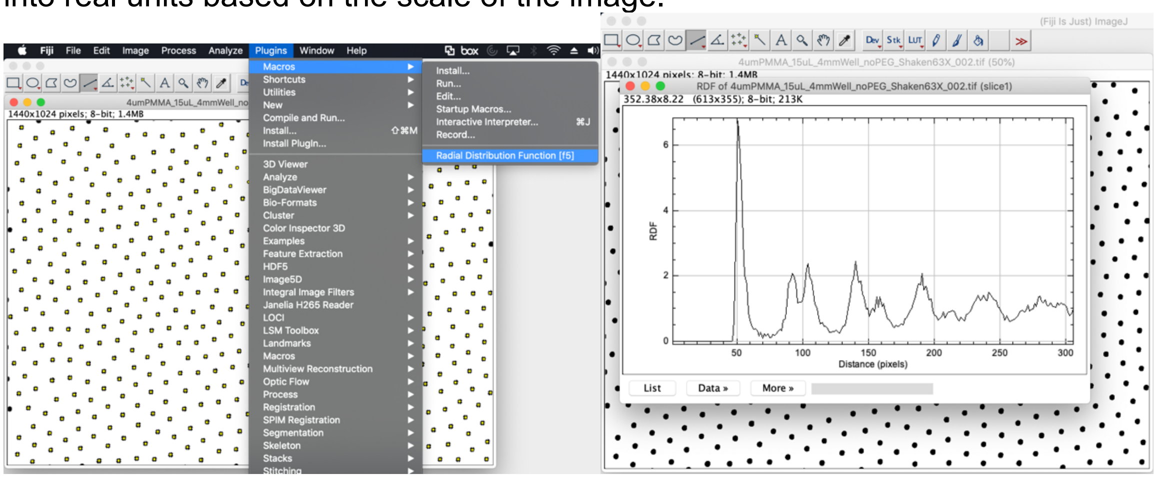

Figure 6: Using the RDF macro to generate an RDF of the image

2.2 Inversion of assembled particles using sol-gel

Sol-gel is a common method of producing a metal oxide. In general, this method is useful in creation of thin films, powders, fibers, and particles with a wide variety of applications. In this project, a silica forming chemistry is used to invert the assembled particles into a structure with fine struts left between the gaps of microparticles. This method was chosen due to its simplicity and repeatability. After application of the sol-gel, the samples consist of microparticles with a coating of silica; in order to have an inverse structure, the particles must be removed from the sample. The removal of particles in this project is done through burning or ashing out the polymer particles. This is done by placing the structure at a temperature well above the thermal degradation temperature of the polymer (PMMA) which removes the polymer and leaves only the silica.

2.2.1 Synthesis and Hydrolysis of Sol-Gel[2]

1.) Combine 7.5mL Ethanol, 1.15mL TEOS, 0.9mL DI H2O, and 65μL 37 wt% HCl in a 50mL vial with a magnetic stir bar
2.) Stir the solution on a hotplate (at room temperature) for *precisely 1 hour* at 300 rpm
3.) Using a 10μL pipet, drop 5μL of solution into the 4mm well with assembled particles (this volume can be varied for different densities)
4.) Bake at 50°C for 48 hours
5.) Remove PDMS well

2.2.2 Removal of Particles by Calcination

1.) Ramp control heat to 500°C by 1°C per minute
2.) Wait 5 hours
3.) Ramp control down to room temperature by 2°C per minute

2.3 Using positive photoresist (AZ4620 or SPR 220-7) on the Nanoscribe
Templating substrates are a promising method to create order colloidal self-assembly. This is crucial to initial nucleation and subsequent assembly of particles. In this case, the Nanoscribe is used in order to create templated substrate through the photosolubility of a positive resist (AZ4620 or SPR 220-7). This allows for the inverse structure to be fabricated using the same 2-photon lithography system, but in an oil immersion configuration. The method is chosen in order to have full flexibility in the templated structure (as opposed to lithography or etching, in which only certain geometries can be created).

2.3.1 Oil immersion configuration for Nanoscribe
Oil immersion is one configuration used with positive photoresist and is desired because it uses an index matching fluid between the objective and the bottom of the substrate (in this, we use ITO covered coverslip). In this configuration, the stack is the following (from the top to bottom): positive photoresist, substrate, oil, objective.

1.) Load the objective of choice into the objective turret
2.) Attach the substrate of choice on the sample holder, with the photoresist facing upward towards the ceiling (Top side) (this is the opposite of the standard Dip-in method)
3.) Add a droplet of Zeiss immersion oil on the substrate side without the photoresist (Bottom side)

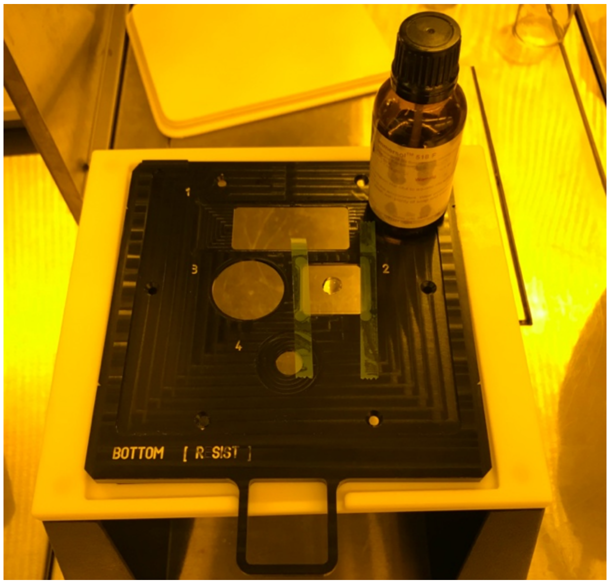

Figure 7: Deposition of immersion oil on the BOTTOM of the substrate

4.) Insert the sample holder so that the oil is facing the objective (top side up)

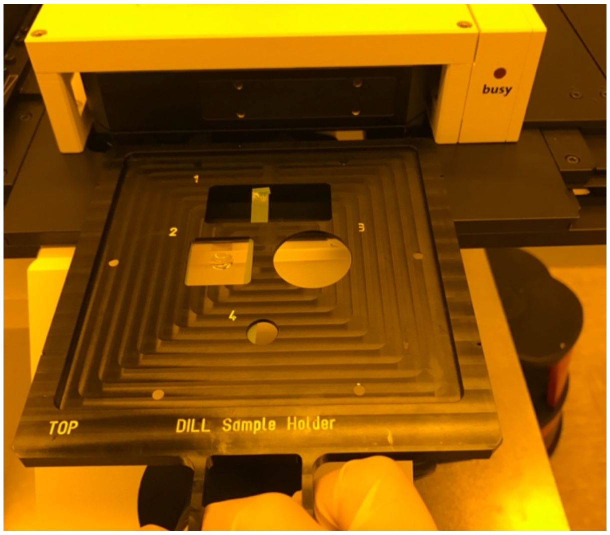

Figure 8: Inserting holder into the Nanoscribe with the oil facing towards the objective

2.3.2 Preparing and loading substrate with positive photoresist (AZ4620 or SPR 220-7)

1.) Prime the substrate using YES Oven standard recipe
2.) Using a syringe, deposit AZ4620 or SPR 220-7 onto the substrate while it is loaded on the spin coater but before starting the spin recipe (over saturating the sample is better than under saturating)

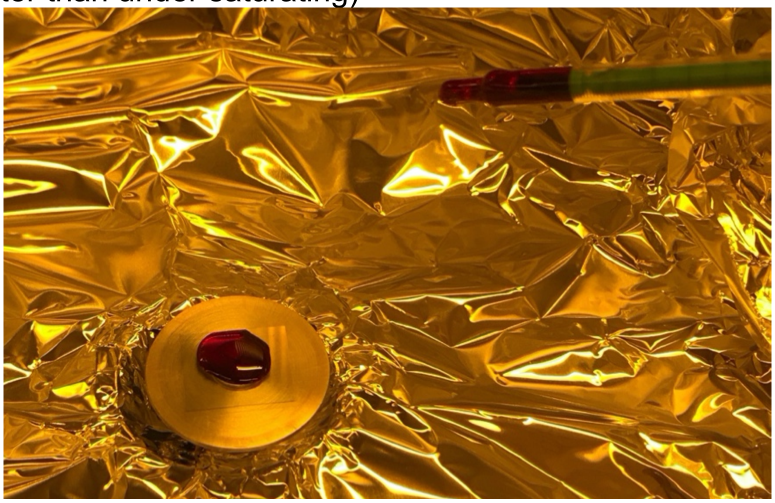

Figure 9: Deposition of SPR 220-7 onto a substrate with a syringe

3.) Ramp control spin coating to 3500 RPM at 250 rpm/s for 2 minutes
4.) Ramp control spin coating to 0 RPM at 500 rpm/s
    a. This should give you ~7 um coating for both AZ4620 and SPR 220-7
5.) Visually inspect to ensure that the substrate is fully coated
6.) Prebake the substrate on a hotplate at [**AZ:** 90C for 90s or **SPR:** 115C for 90 seconds]
7.) Remove and load the substrate into the Nanoscribe using the oil immersion configuration (from 2.3.1 procedure)

8.) Use standard operating procedures to find the interface, making sure that the correct interface is detected (in this case, there are many interfaces: air-oil, oil-substrate, **substrate-photoresist**, and photoresist-air)

2.3.3 Programming a dosing matrix

1.) Open Describe and File >> Advanced STL Processing

2.) Click the tab with “Parameter Sweep”

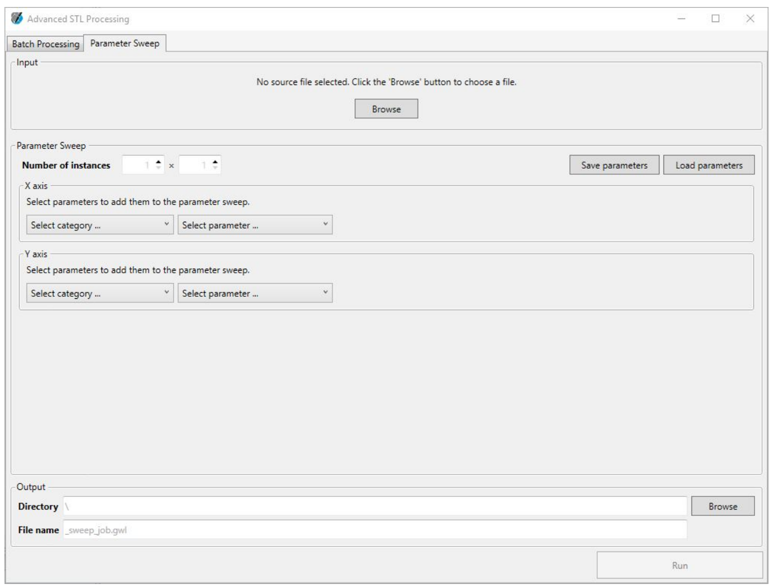

Figure 10: Parameter Sweep tab in the Advanced STL Processing menu

3.) Input a STL of a shape to be printed by “Browse” (usually a smaller, representative geometry of the final print)

4.) Change the “X axis” by “Select category …” and “Select parameter …”

   a. Category: Exposure, Parameter: BaseLaserPower

5.) Change the “Y axis” by “Select category …” and “Select parameter…”

   a. Category: Exposure, Parameter: BaseScanSpeed

6.) Change the number of columns or rows by changing “Number of instances”, which is found at the top of the “Parameter Sweep” box.

7.) Change the initial and end values, with how to interpret those values, by further expanding the option with the arrow next to your selected category and parameter

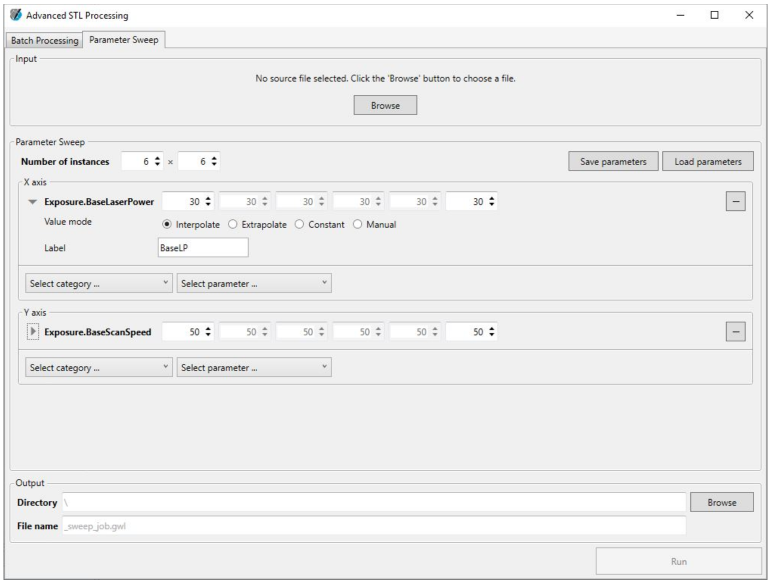

Figure 11: Paramter Sweep tab with the Exposure.BaseLaserPower and Exposure.BaseScanSpeed as the variables in 2 directions (X,Y)

8.) Click “Run” after finalizing
9.) For oil immersion mode, change InvertZAxis 1 to InvertZAxis 0
10.) Change “% Text parameters”
    a. TextScanSpeed 1000 to TextScanSpeed 10000
    b. TextLaserPower 55 to TextLaserPower 40

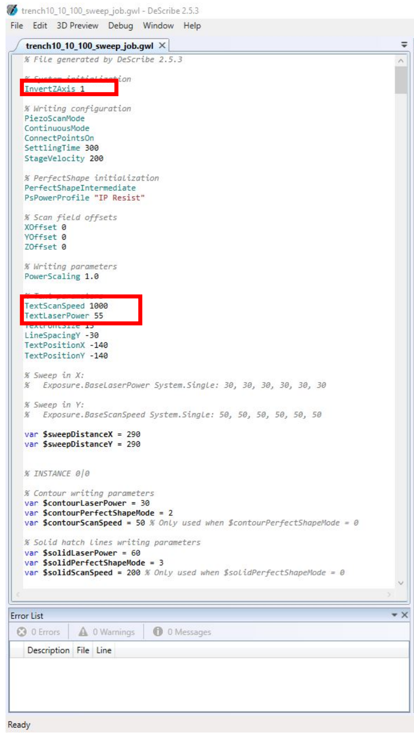

Figure 12: .GWL file generation after STL processing showing regions of code that need to be changed per Step 10

11.) Save the file and load/run the program in Nanowrite

2.3.3 Post processing positive photoresist

1.) Develop the substrate in [**AZ:** AZ400K Developer:water = 1:4 dilution or **SPR:** MF-26A] for 120 seconds with slow agitation
2.) Wait 30 minutes
3.) Post bake at [**AZ:** 125C for 30 minutes or **SPR:** 115C for 30 minutes]

References

1. Baggethun, Paul. ImageJ radial distribution file: https://imagej.nih.gov/ij/plugins/radial-profile.html. Based on a guide: https://imagejdocu.tudor.lu/macro/radial_distribution_function
2. Zhang, Xiaoran, and G. J. Blanchard. "Polymer Sol–Gel Composite Inverse Opal Structures." *ACS applied materials & interfaces* 7.11 (2015): 6054-6061.

Supplementary

PDMS wells on silicon

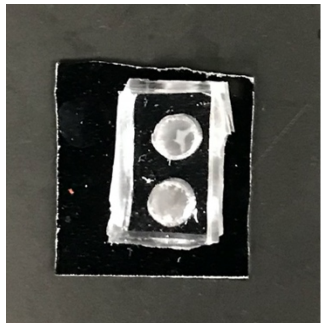

Figure 13: PDMS well adhered to a silicon substrate through air plasma treatment

Self-assembly of monolayer of PMMA

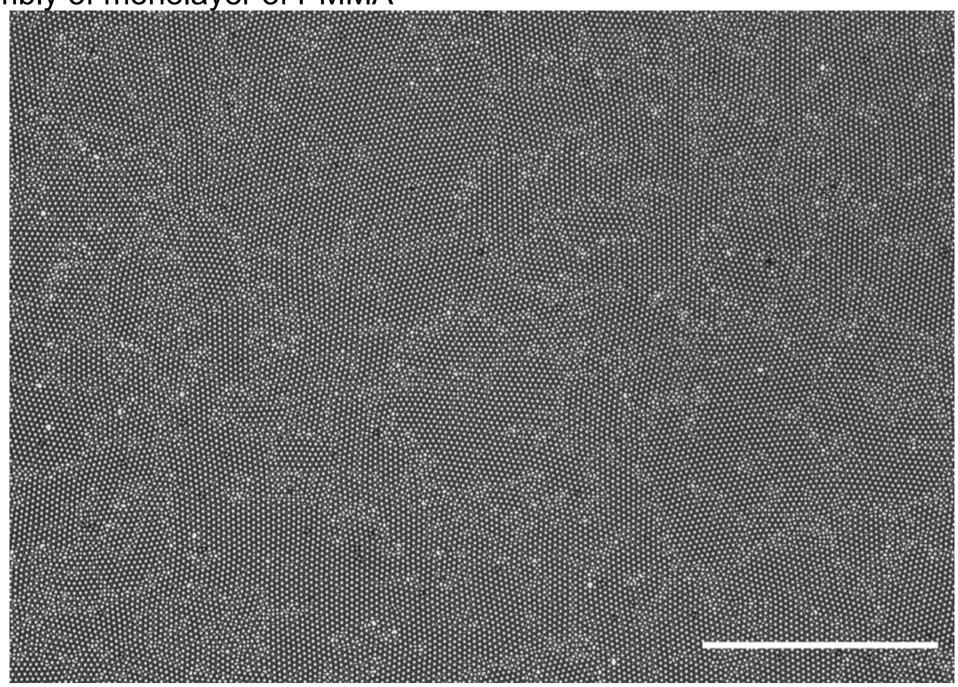

Figure 14: Optical image of monolayer of 4 um PMMA using the SOP. Scale bar is 40 um.

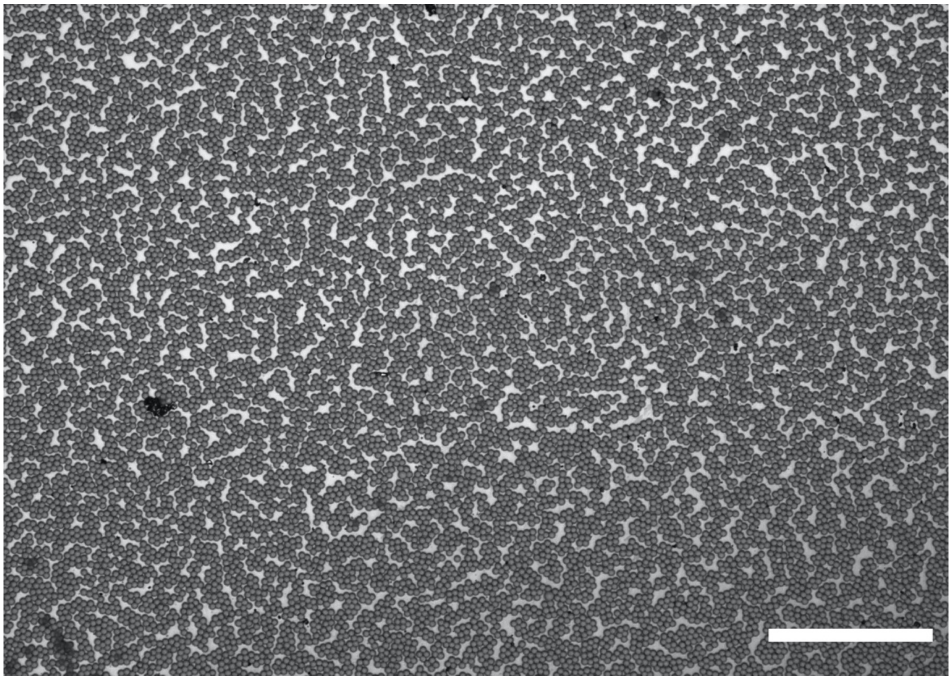

Figure 15: Optical image of monolayer of 4 um PMMA in a well without SOP. Scale bar is 100 um.

Inverted Self Assembled Structure

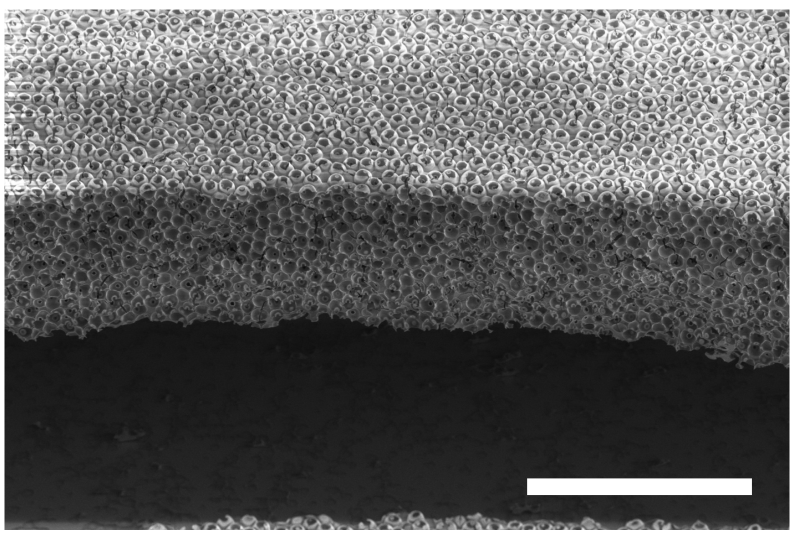

Figure 16: SEM image of an SiO_2 inverted structure using the SOP (tilted at 45 degrees). Scale bar is 50 um.

RDF of Inverse Structure

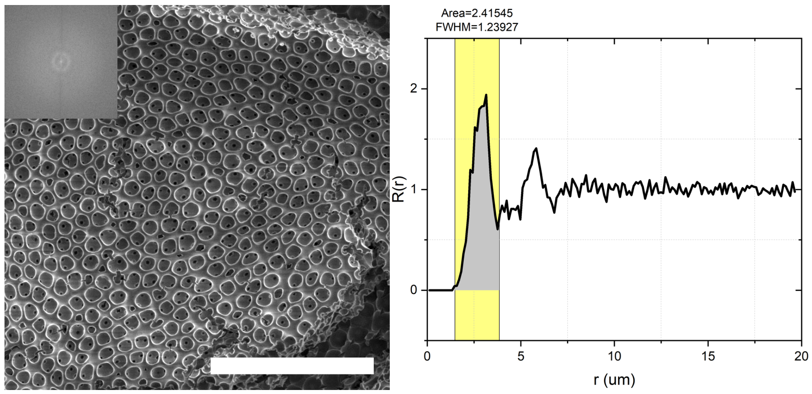

Figure 17: (left) SEM image of an SiO_2 inverted structure that is disordered with its FFT in the top left. Scale bar is 50 um. (right) RDF generated using SOP showing the FWHM and area under the curve.

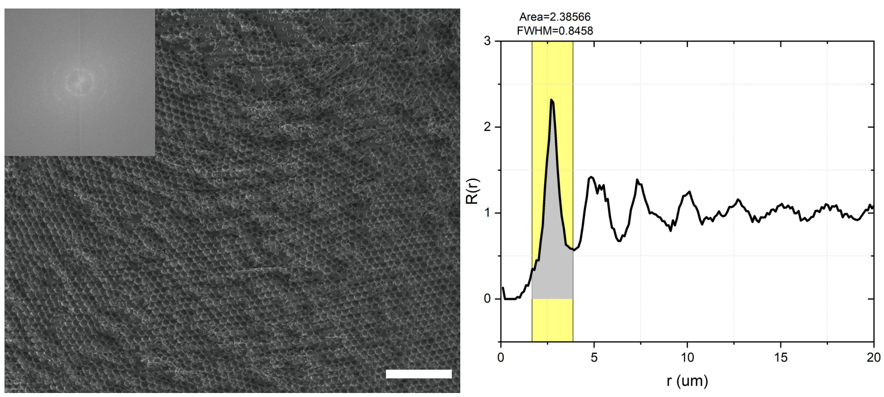

Figure 18: (left) SEM image of an SiO_2 inverted structurewith its FFT in the top left. Scale bar is 50 um. (right) RDF generated using SOP showing the FWHM and area under the curve.

Dosing Matrix for AZ4260

Scan Speed x 10^2 (μm/s)

Laser Power (%)	10	57.5	105	152	200
20	+	+	–	–	–
40	x	+	+	+	+
60	x	x	+	+	+
80	x	x	x	x	x
100	x	x	x	x	x

Table 1: Dosing matrix for AZ4260 showing under exposed (-), well exposed (+), or over exposed resist (x).

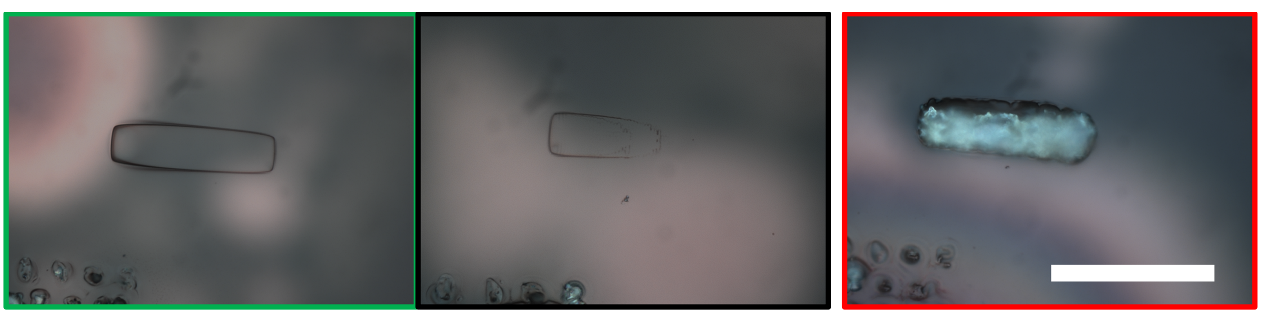

Figure 19: All images are of AZ4620. (left) Optical image of well exposed condition. (middle) Optical image of under exposed condition. (right) Optical image of over exposed condition. Scale bar is 100 um.

Dosing Matrix for SPR220-7

Scan Speed x 10^2 (μm/s)

Laser Power (%)

	50	70	90	110	130
36	+	+	–	–	–
42	+	+	+	+	–
48	x	+	+	+	+
54	x	x	+	+	+
60	x	x	x	+	+

Table 2: Dosing matrix for SPR 220-7 showing under exposed (-), well exposed (+), or over exposed resist (x).