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.

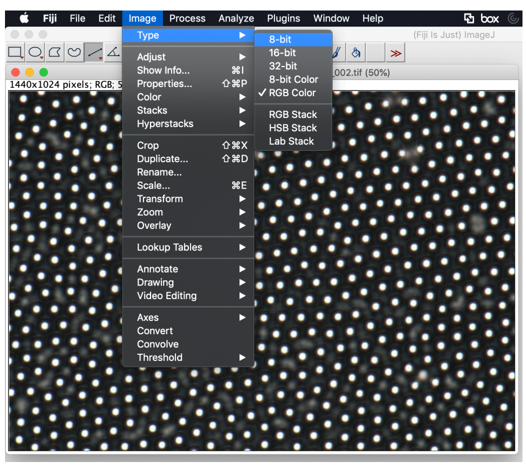

Figure 1: Converting image into an 8-bit through ImageJ

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

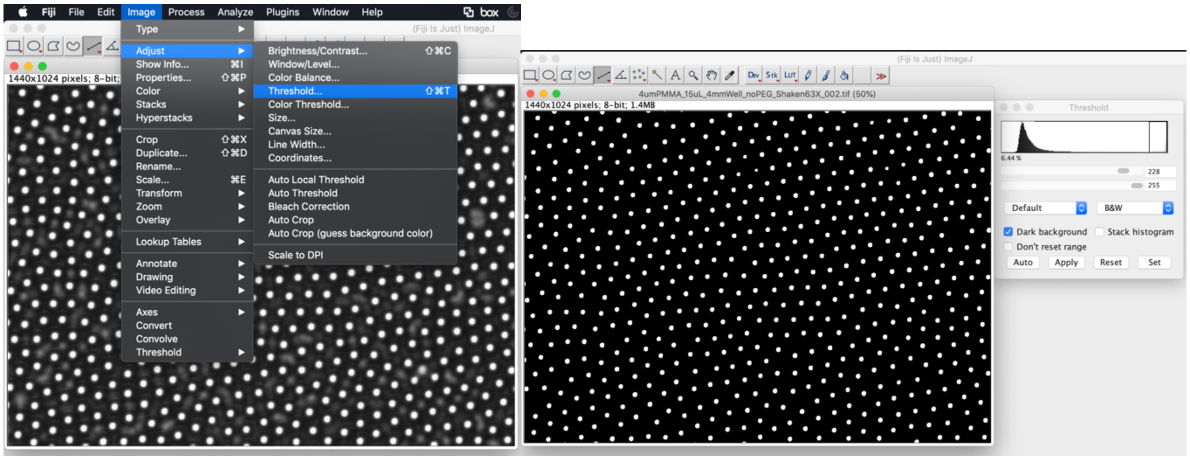

Figure 2: Thresholding an image to get binary data in ImageJ

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

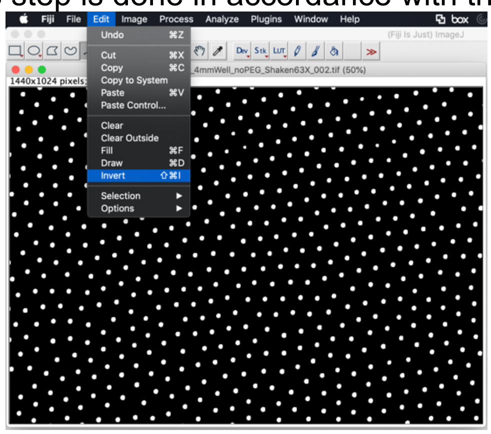

Figure 3: Inverting the binary image in ImageJ

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.

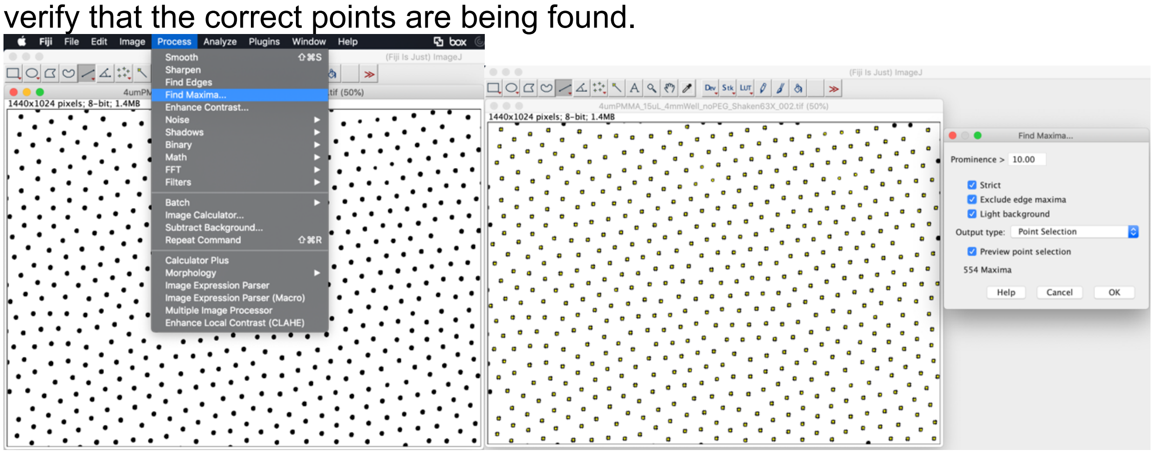

Figure 4: Finding points within the binary data for calculation of RDF in ImageJ

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

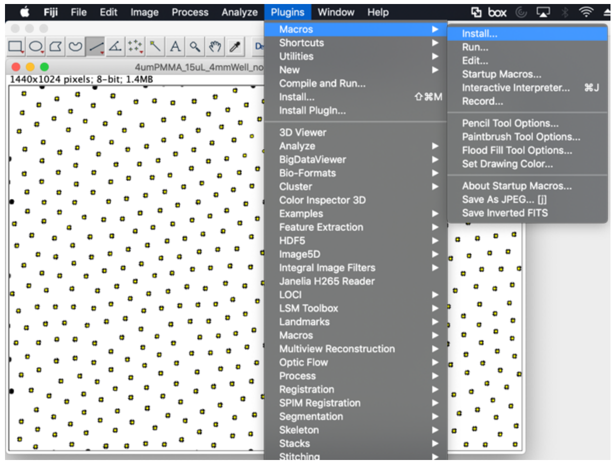

Figure 5: Installing a macro function for RDF generation

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.

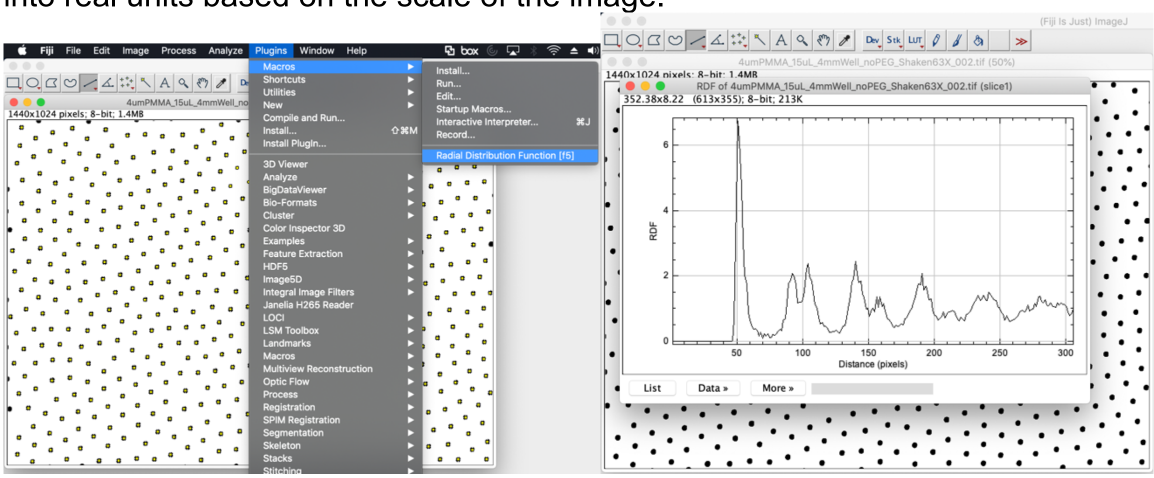

Figure 6: Using the RDF macro to generate an RDF of the image

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

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

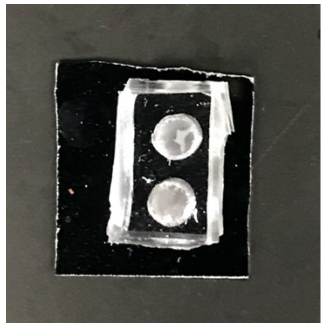

Figure 13: PDMS well adhered to a silicon substrate through air plasma treatment

Self-assembly of monolayer of PMMA

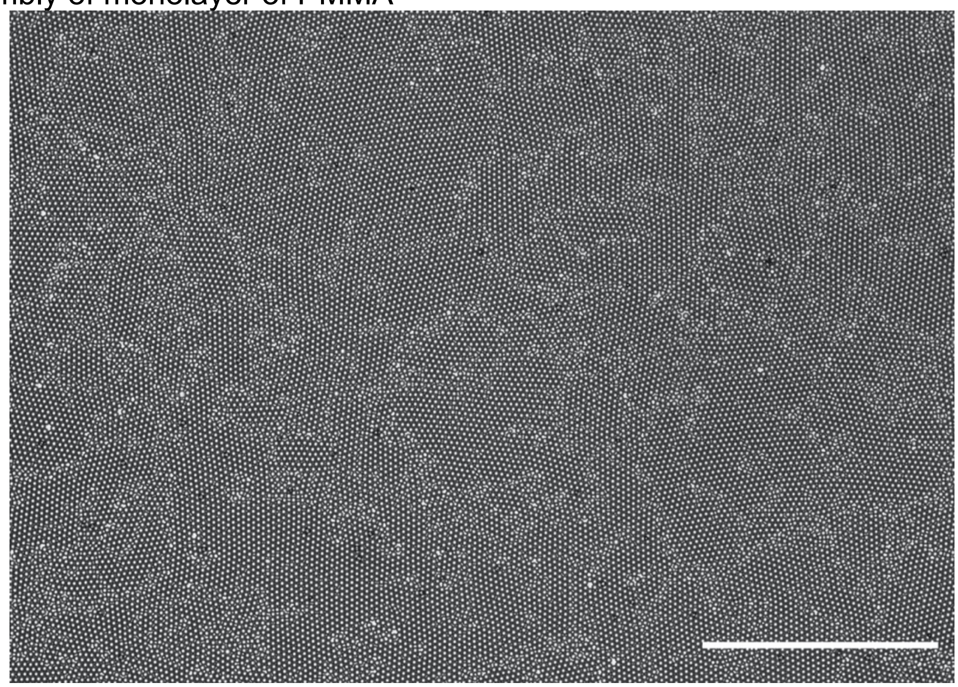

Figure 14: Optical image of monolayer of 4 um PMMA using the SOP. Scale bar is 40 um.

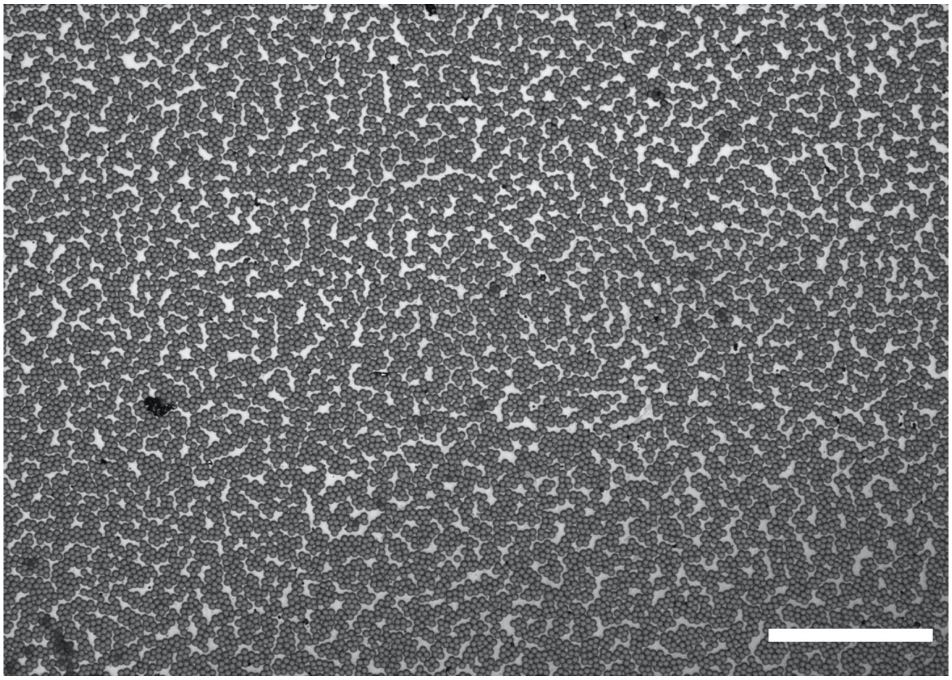

Figure 15: Optical image of monolayer of 4 um PMMA in a well without SOP. Scale bar is 100 um.

Inverted Self Assembled Structure

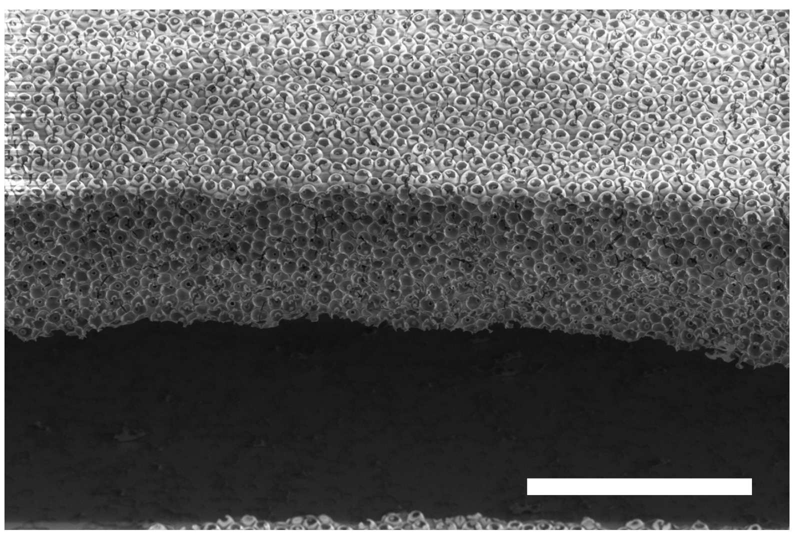

Figure 16: SEM image of an SiO_2 inverted structure using the SOP (tilted at 45 degrees). Scale bar is 50 um.

RDF of Inverse Structure

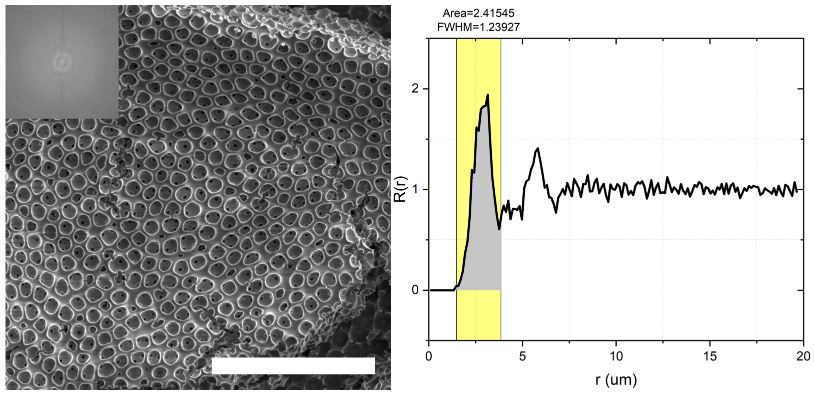

Figure 17: (left) SEM image of an SiO_2 inverted structure that is disordered with its FFT in the top left. Scale bar is 50 um. (right) RDF generated using SOP showing the FWHM and area under the curve.

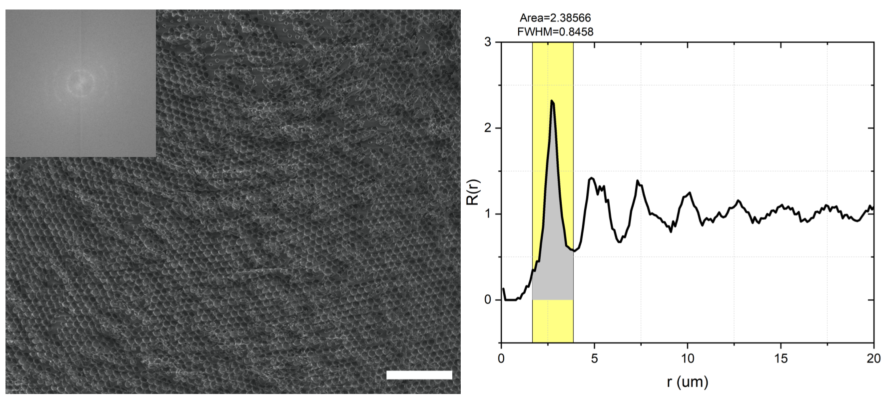

Figure 18: (left) SEM image of an SiO_2 inverted structurewith its FFT in the top left. Scale bar is 50 um. (right) RDF generated using SOP showing the FWHM and area under the curve.