

Facile Assembly of Functional Materials using Lithographically Controlled Wetting

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INTRODUCTION

Control of the assembly of colloidal particles with spatial selectivity across large-scale areas is of interest in emerging applications such as chemical sensors and photonic devices. Current lithographic techniques such as electron beam lithography are commonly employed to prepare nanofeatures and microstructures for such devices. This technology continues to advance, but proves to be very expensive and time consuming for practical applications. It is also suited for patterning only a small list of materials. Recent studies have highlighted techniques to systematically pre-select and produce patterns by exploiting capillary-bridge forces generated in geometrically confined structures.^{1,2} Such techniques include dip-pen nanolithography (DPN)³, confined dewetting⁴, and lithographically controlled wetting.²

Recently, we have developed a new nontraditional lithographic technique, termed confined dewetting lithography (CDL) that shows promise for patterning a variety of nano-sized components (spheres, particles, rods) on a multitude of surfaces. This approach is particularly attractive in that the lithographic template is low-cost and reusable. Furthermore, the patterning occurs within seconds to minutes without need for use of expensive lithographic agents or instruments. Using polystyrene (PS) microspheres as a model colloid we elucidated the optimal conditions where CDL has a high efficiency in fabricating patterned structures of many sizes and shapes. We offer specific applications of this method by showing the quick assembly of iron oxide particles for the growth of carbon nanotube structures and the assembly of magnetic particles for a variety of uses.

ASSEMBLY OF MICROSTRUCTURED ARRAYS USING CDL

Protocol

A pair of home-constructed cells were used for the micropatterning of colloidal polystyrene microspheres. The cells were constructed to eliminate the convective flow of particles to a pinned contact line observed when simply drop-casting a droplet of solution on a given substrate. With a confined area for patterning, reproducibility of the assembled microstructures was greatly increased.

An overview of the assembly process can be seen in figure 1. The cell is assembled using either clean ITO coated glass slide or a silicon wafer. A 1 – 20 mL aliquot of 1% wt polystyrene microspheres in water of differing diameters ranging from 64 nm – 2 μ m are then applied into the cell, wetting the walls of the washer or O-ring used to define the patterning area. A microgrid, consisting of a TEM grid or metal sieve, is then placed over the solution and floats atop the solution. After a specified time of 10 – 30 minutes the water of the solution evaporates fully and the microgrid can then be removed. After subsequent removal of the microgrid, an exact replica of the template is

observed with the same dimensions as the grid. Interesting structures can also be formed from mixtures of microspheres with varying diameters showing an even higher degree of ordering.

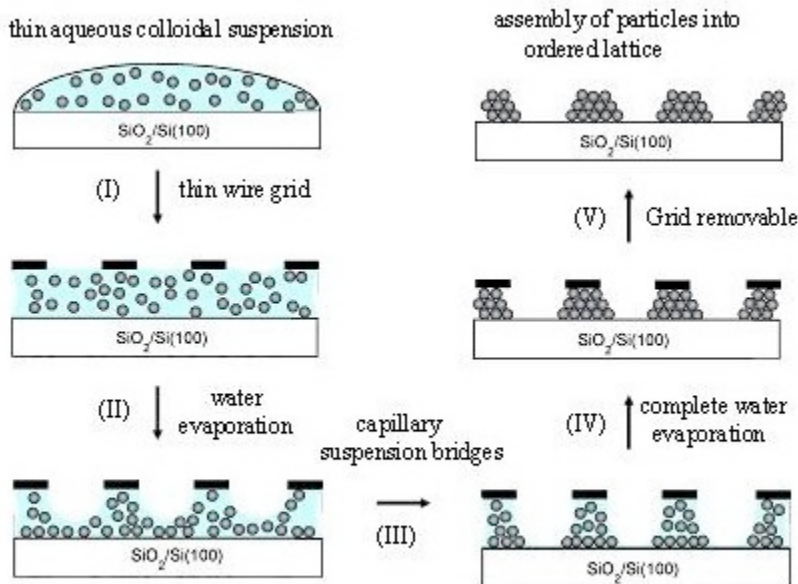
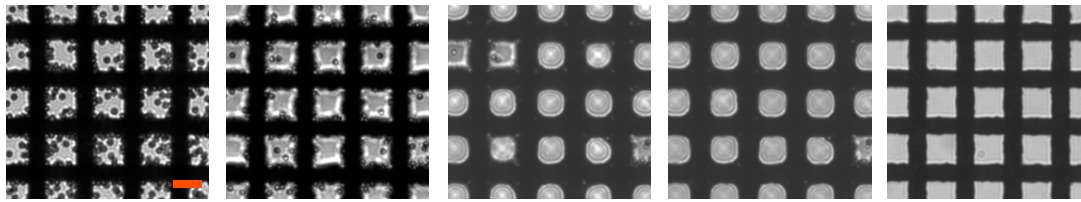


Figure 1

Optical images of the evaporative process can be seen in figure 2. The particles move during the early stages of evaporation by brownian and thermal motion. As the solution evaporates capillary bridges can be observed forming between the grid and the substrate. These unpinned contact lines then act to draw the particles in the solution underneath the features of the microgrid due to convective, capillary, and Plateau border forces. After total water evaporation, a majority of the microspheres have been drawn underneath the features. The exact replica of the template is observed after removal of the microgrid.

Determination of Optimal Patterning Conditions

By studying the forces contributing to the assembly of the structures the optimal conditions were then exploited for constructing arrays of particles at the nano dimension. As current methodologies aim to the smaller and smaller size domains, our scheme poses a simple way to exploit such gravitational and electrostatic forces to assemble such structures by simply altering the substrate-particle interactions.



scale is 10 μm

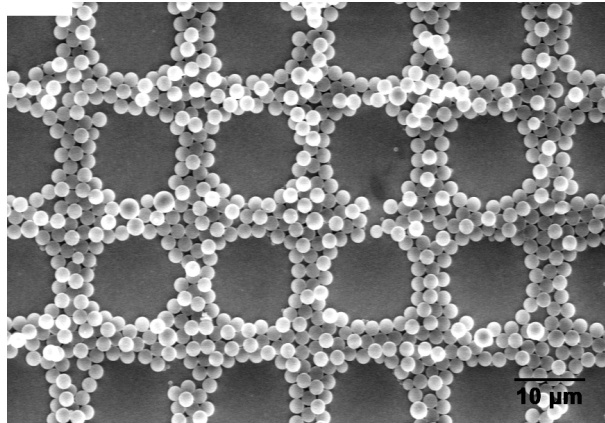
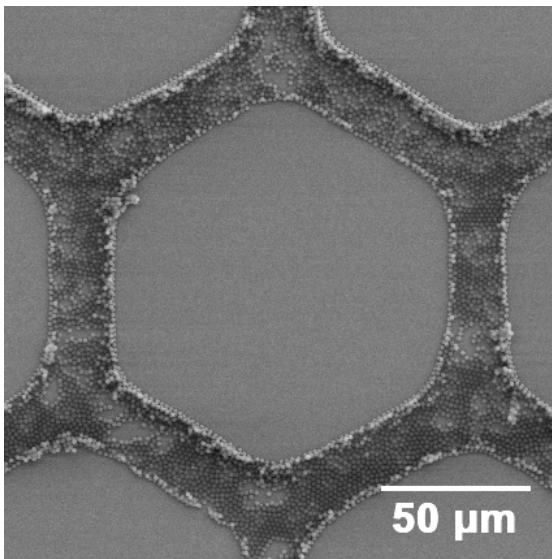
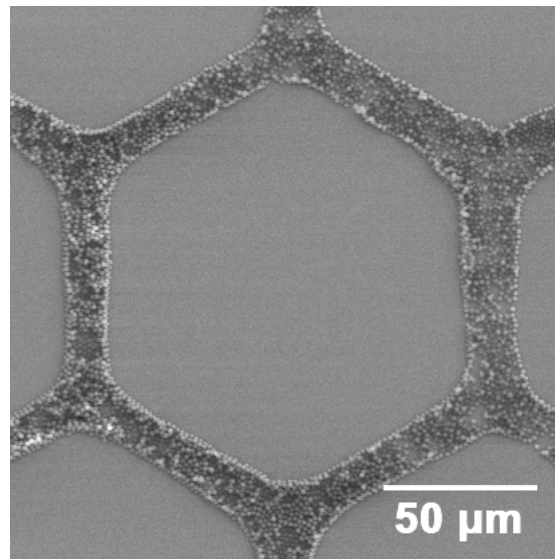


Figure 2

Figure 3 shows SEM images of hexagonal patterns on a native SiO₂ commercial wafer cleaned in piranha solution, 3:1 v/v H₂SO₄:H₂O₂. In all experiments 1 mL of 1 wt % 1.71 μm polystyrene microspheres suspended in water were applied to the home constructed TEM grid cell. It is interesting to see that gravitational effects do not affect the patterning process as the cell is either inverted or non-inverted as related to the gravitational direction. As observed, no particles remain in the holes of the patterns, but are all deposited under the features of the hexagonal template for a clean pattern.



Inverted cell

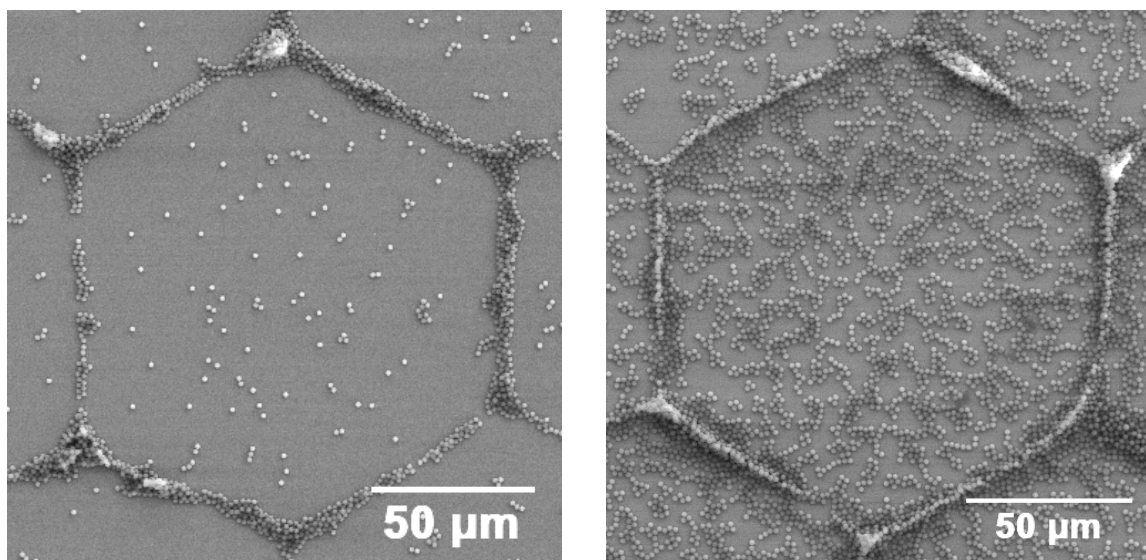


Non-inverted cell

Figure 3

Positive Surface-Particle Interactions

Considering the negative surface charges of the sulfonate groups of the polystyrene microspheres in aqueous solution, the effects of electrostatic forces between the microspheres and modified surfaces were explored. To create a positive electrostatic interaction between the substrate and the microspheres a positively charged substrate was prepared. To prepare a positively charged substrate a 5 wt % 3-aminopropyl-trimethoxysilane was spin-coated onto a clean native SiO₂ substrate.^{5,6} Through many condensation reactions between the silane and the SiO₂ a chemical bond is formed with the first layer of silane. Subsequent rinsing with water leaves approximately 1/2 monolayer coverage. In aqueous solution, the modified substrate should have protonated amine groups of positive charge.



Inverted cell

Non-inverted cell

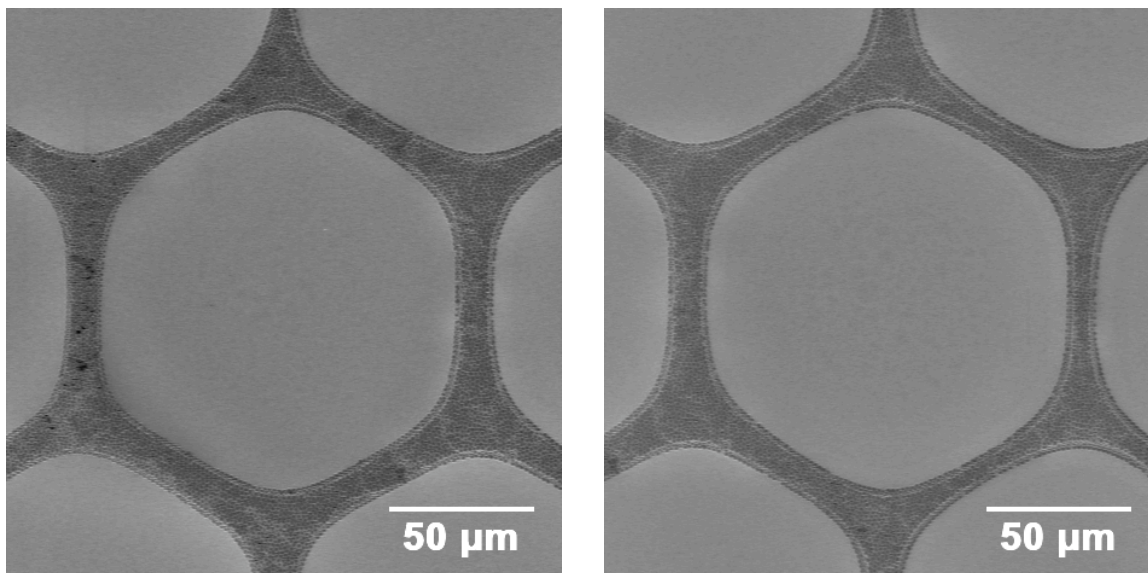
Figure 4

The SEM images of figure 4 show the effects of the silane modified substrate. Since the polystyrene microspheres have negatively charged sulfate surface groups they should be attracted to the positively charged substrate. The attractive interactions lead to poorer patterning than on a clean SiO₂ substrate. Also here gravitational effects play a role in the patterning process not observed on clean wafers. It is assumed that gravitational force coupled with electrostatic force is large enough to be equivalent to the capillary and convective forces leading to the patterning of the microspheres.

Negative Surface-Particles Interactions

The effects of the repulsive forces between the negatively charged polystyrene microspheres and a negatively charged substrate were also explored. To obtain negatively charged substrates we evaporated a thin layer of chromium followed by gold onto a clean SiO₂ wafer. Using a well known procedure, the gold substrate was soaked in a 1mM 16-mercaptohexadecanoic acid ethanol solution for ~ 1 min to obtain monolayer

coverage of the carboxylic acid thiol.⁷ In aqueous solution it is assumed that the carboxylic acid end group should be deprotonated and the substrate negatively charged.



Inverted cell

Non-inverted cell

Figure 5

It is assumed that the negatively charged sulfate surface groups on the polystyrene microspheres should repulsively interact with the surface of the negatively charged carboxylic acid thiol modified substrate. Thus the microspheres should not be attracted to the substrate and the capillary and convective forces leading to the patterning of the spheres should have little resistance from substrate-polystyrene attractive electrostatic forces. The SEM images in figure 5 on the left show very clean patterns with all microspheres patterned under the features of the hexagonal TEM grid.

These effects were exploited to the patterning of very small spheres in the nanometer range. On bare SiO₂ the capillary bridging forces acting to draw the particles under the features of the floating microgrid are unable to move such small spheres, leading to poor pattern formation. The use of the thiol modified substrates, however, leads to uniform patterns that exhibit a robust diffraction pattern, signifying long range periodicity. Figure 6 shows the using of these thiol modified substrates, elucidating the effects of modified substrates for the patterning of smaller particles. A clean pattern is observed when these forces are considered and exploited.

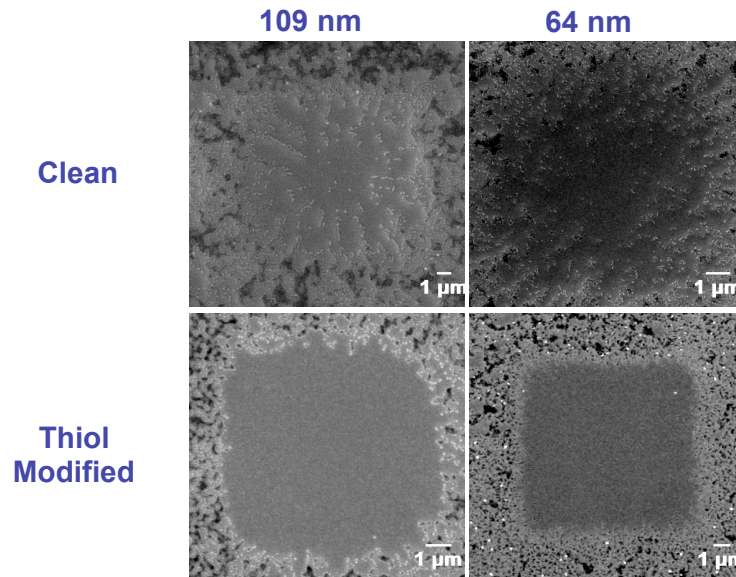


Figure 6

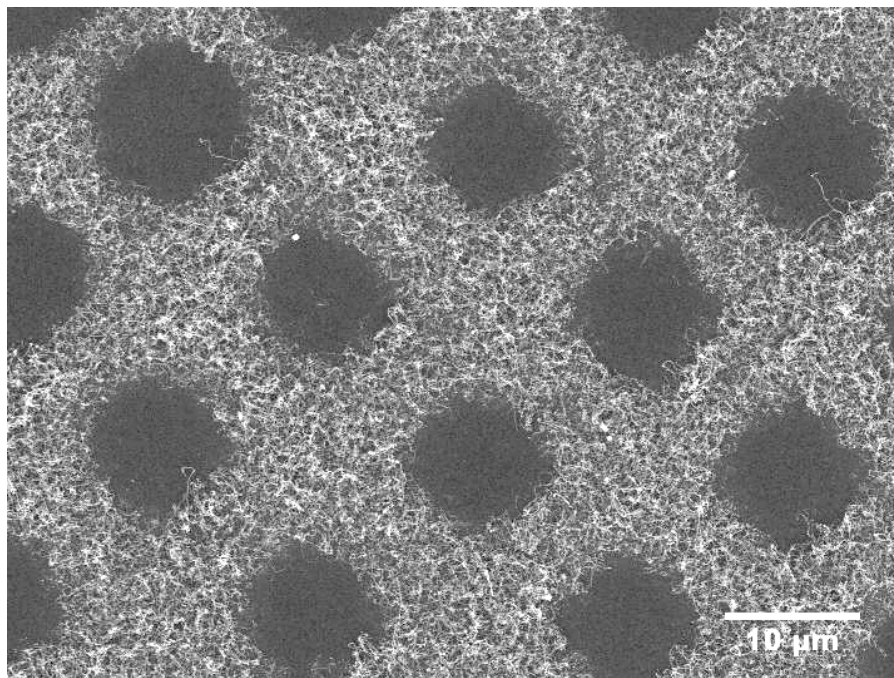


Figure 7

EXPLOITING CDL FOR CARBON NANOTUBE INTERCONNECTS

Iron oxide 3nm Nanocat™ particles have been patterned easily using our technique. The particles were assembled on SiO₂(200 nm)/Si wafers via CDL. The subsequent growth of carbon nanotubes under controlled vapor deposition (CVD) led to the formation of a periodic array of the fibers. Under a stream of Ar and H₂ a carbon precursor such as xylene or pyridine is injected into F1 at 130-150°C. The patterned iron

oxide sample is positioned in F2 at 700-900°C.⁸ The iron oxide seed particles undergo pyrolysis to form a carbon nanotube array as seen in figure 7.

Such structures could be employed as interconnects in electronic devices. CDL offers promise as a facile, low cost method for the assembling interconnect structures. By choosing the precursor carbon source nanotube arrays of specific functionalities can also be formed which have interesting properties that can be exploited in electronic schemes.

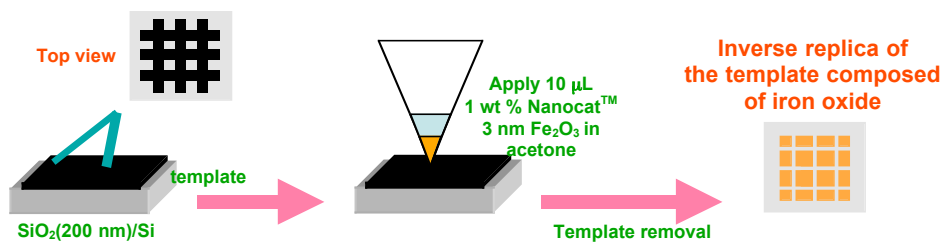


Figure 8

Modified CDL for obtaining inverse template structures

The schematic in figure 8 shows our modified CDL method for making inverse template structures. Using this method a template is placed flat against the silicon substrate. An acetone solution containing iron oxide nanoparticles is applied to the template and allowed to dry. After removal of the template an inverse replica of iron oxide nanoparticles is obtained. This method yields extremely high domains and is highly reproducible. We have found that only the acetone mixture leads to the formation of these inverse-only templated structures. The nanoparticle arrays can then undergo the same CVD treatment to yield carbon nanotube structures. An example of a long range ordered structure using this method can be seen in figure 9.

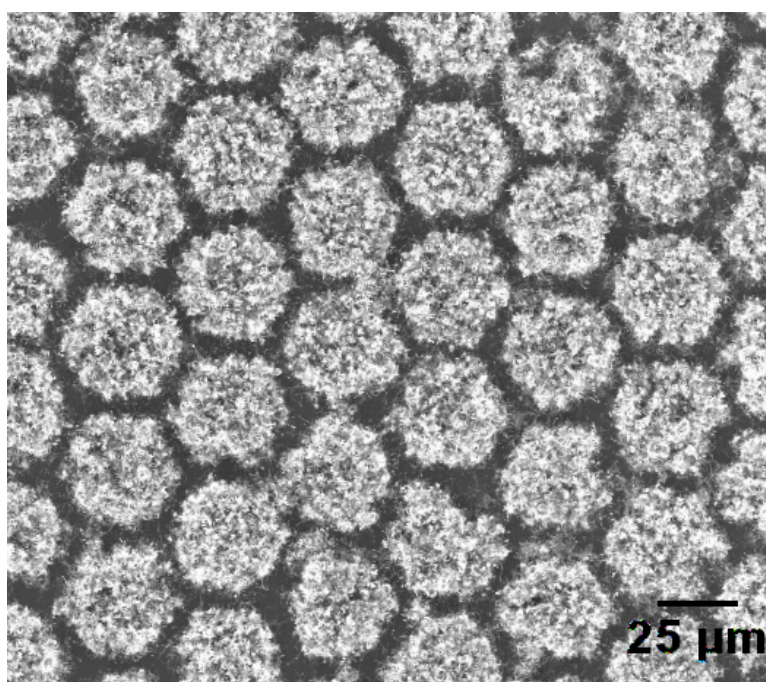


Figure 9

USING CDL FOR ASSEMBLY OF MAGNETIC ARRAYS

Magnetic microarrays are commonly used in many systems such as for sensing devices and electronic materials. For our uses we are interested in making magnetic arrays of a certain periodicity to explore these effects on electrochemical electron transfer kinetics. Specifically, the effects of magnetic fields at the electrodes of batteries have been exploited for years as a means to increase the current output and performance. Yet there is still much to understand on the nature of these interesting effects. For use in such basic and acidic environments as with batteries the magnetic particles typically employed to produce such magnetic fields must be coated with an inert substance to prevent corrosion and leaking. Little progress has been made in the coating of permanent magnetic particles such as NdFeB.

NdFeB is a permanent magnetic material possessing a high residual induction commonly used in such applications. We have recently sought to chemically coat these particles to be using in producing such magnetic arrays for electrochemical studies. Spherical NdFeB particles were obtained from MagnequenchTM. Our procedure aims to coat the particles with an inert material of polystyrene. The particles are first treated with a vinyl silane to chemically attach to the surface of the particles. A polystyrene polymerization is then completed under constant agitation of the particles chemically attaching the polymer nuclei to the vinyl groups and the positive charged surface of the magnetic particles. Figure 10 shows the SEM images of the particles before and after the coating procedure. The charging of the particles in the right image shows the nonconductive polystyrene surface of the particles.

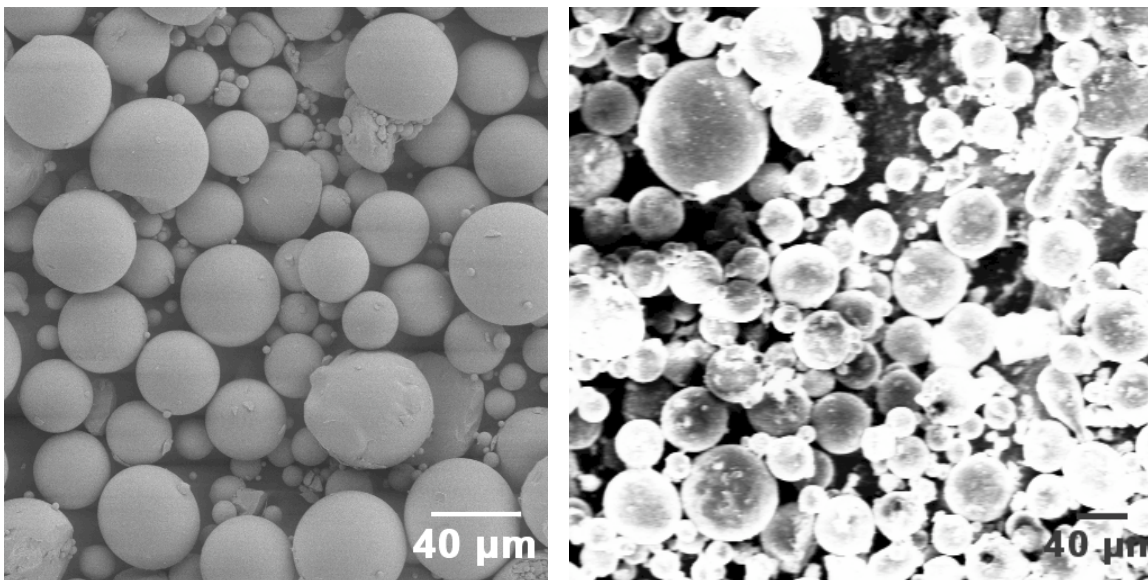


Figure 10

CONCLUSION

We demonstrated the use of an array of localized dewetting processes to assemble colloidal PS particles into square and hexagonal patterns on various solid substrates. Our method is relatively easy and inexpensive to set up on a bench top under ambient

conditions. It allows for a fast and highly efficient patterning process of micron-sized PS colloidal particles on relatively large areas of ITO/glass, other similar oxide substrates, and negatively charged substrates. For the sub-micron PS colloidal particles, it was necessary to negatively functionalized the substrates to effectively assembly square and hexagonal particles with no or a few PS particles in the holes of the patterns. Choosing the appropriate conditions and materials, in principle, our approach paves the way to virtually any geometric colloidal pattern including the patterning of nanometer size iron oxide particles for growth of carbon nanotube arrays, and the patterning of magnetic particles for a certain periodicity.

We are currently submitting an article to *Langmuir* detailing our experiments on CDL. We hope to compose a short article discussing our method for producing arrays of carbon nanotubes of different compositions, and we are preparing a manuscript discussing our method for the polymer coating of NdFeB particles.

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