Electronic Supplementary Information

1. Experimental procedures and ellipsometry data reduction

PDMS elastomer is made by mixing Sylgard^{TM} 184 base and the curing agent in a 10:1 ratio and pouring the mixture onto a cut and cleaned silicon wafer in a Petri dish. The mixture is then cured by baking at 80 ^{0}C for 2 hours on a hot plate. Once cured, the PDMS is peeled from the wafer and then cut into 1 cm × 1 cm pieces.

A 30 wt% colloidal dispersion of 27 nm LUDOX® TM-50 silica nanoparticles (SiO_2 NP) is obtained from Sigma Aldrich. A 15 wt% dispersion is prepared by diluting with de-ionized water and the dispersion is sonicated for 5-6 hours. 1 cm × 1 cm silicon wafer pieces cleaned with isopropanol, acetone, and water and then plasma cleaned for 4-5 minutes. The NP suspension is then spin coated on the silicon wafer substrate using a Laurell Technologies Co., WS-400BZ-6NPP/Lite spin coater with the spin conditions set at 2000-2500 rpm for 1.5 minutes. The thickness and refractive index of the NP packings are measured using an Alpha-SE spectroscopic ellipsometer from J.A. Wollam using a wavelength range of 370-900 nm. The source incidence and detection angles are set at 70° relative to normal incidence.

A simple Cauchy model is used to fit the ellipsometry data to calculate the film properties.[1] The Cauchy model describes the dependence of refractive index on wavelength as:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

where A, B and C are parameters that are used to fit the data to the model. Additional parameters like k-value, exponent, and angle offset are used to improve the quality of fit.

By describing the film composition using a simple volume-mixing argument, we can deduce the amount of oligomers in the packing. The estimation of the volume fraction of oligomers in a NP film is performed by expressing the refractive index as a simple sum of the product of refractive indices of the constituents of the film and respective volume fractions of the components. For the neat NP film, we have:

$$n_0 = 1.475\varphi_{NP} + 1.33\varphi_{Water} + (1 - \varphi_{NP} - \varphi_{Water}) \qquad (1)$$

where φ_{NP} is the volume fraction of NP in the packing and φ_{Water} is the volume fraction of capillary condensed water in the packing.

For the same film after LeCaRI, we have:

$$n_1 = 1.475\varphi_{NP} + 1.33\varphi_{Water} + (1 - \varphi_{NP} - \varphi_{Water} - \varphi_{PDMS}) + 1.430\varphi_{PDMS} \tag{2}$$

where φ_{PDMS} is the volume fraction of PDMS oligomers in the packing. By subtracting (1) and (2), we get the volume fraction of oligomers as:

$$\phi = \frac{n_1 - n_0}{n_{PDMS} - 1} = \frac{n_1 - n_0}{1.432 - 1} \tag{3}$$

The maximum void fraction in the packing is given as:

$$\theta = 1 - \frac{n_0 - n_{air}}{n_{SiO2} - 1} = 1 - \frac{n_0 - 1}{1.475 - 1} \tag{4}$$

The values of refractive indices of SiO_2, air, and PDMS are obtained from references as 1.475, 1, and 1.432, respectively.[2]-[5]

SEM images of the top-down and cross-section of the samples are taken using a JEOL 7500F HRSEM. The sample is sputtered with a 4 nm iridium layer using a Quorom plasma generating sputter coater prior to imaging to prevent charging. Cross-section images are taken by cleaving the sample using a diamond scribe and mounting the sample vertically on a stub with the cross sections facing the beam. An accelerating voltage of 5 kV, emission current 20 μA, at a working distance of ~8 mm is used to image the samples.

2. Design of humidity chamber and data collection for Figure 3

The humidity chamber is constructed by enclosing a Boneco Air-O-Swiss® Ultrasonic Digital Humidifier in a tight chamber. The front wall of the chamber is designed with two inlets for access. A digital humidity sensor Fisherbrand™ Traceable™ Jumbo Thermo-Humidity Meter is used to monitor and measure the humidity inside the chamber.

Commercial SiO_2 suspensions of LUDOX® SM-30(7 nm diameter), LUDOX® TM-50(27 nm diameter) are obtained from Sigma Aldrich, and SNOWTEX® ST-YL(61 nm diameter) and

SNOWTEX® ST-ZL(77 nm diameter) SiO_2 are obtained from Nissan Chemical America Corp. SiO_2 NP films of thickness 250-300 nm are made using spin coating as explained above. The thickness and refractive indices of the films are measured using ellipsometry. The Cauchy model with additional parameters - k-value and exponent, angle offset – is used to fit the data.

These films are exposed to humidity levels of 20-25% relative humidity (RH) under ambient conditions, and 40-45% RH and 55-60% RH in the humidity-controlled chamber. In all cases, the films are allowed to come to equilibrium with the surroundings by waiting for 5 minutes before proceeding further with LeCaRI. PDMS gels are brought into conformal contact with the NP films and left in contact for 15-20 seconds. The PDMS elastomer is then peeled off and the refractive indices of the films are measured using ellipsometry. The refractive index before and after the infiltration is compared to determine the amount of oligomers in the packing.

3. Determination of the amount of capillary-condensed water

The amount of water condensed in the NP films varies with the size of the NP and the humidity level. At room temperature and humidity, we measure the refractive index of NP film. This film is then mounted on a heat stage Linkam THMS350V and ramped up to 150 ^{0}C at a heating rate of 30 ^{0}C/min. The temperature is held at 150 ^{0}C for one hour while the ellipsometric measurement of the film is performed. By comparing the refractive index of the NP film after heating ($n_{RH=0}$ at 0% humidity) to before heating ($n_{RH=22}$ at RH of 22%), we can determine the amount of capillary condensed water using:

$$\theta(at\ RH = 22) = \frac{n_{RH=22} - n_{RH=0}}{n_{water} - 1} = \frac{n_{RH=22} - n_{RH=0}}{1.33\ - 1} \qquad (5)$$

By repeating the same for relative humidity value of 38%, we can estimate the amount of water condensed in the NP film at RH 38%. The amount of water condensed in the NP films is shown in Figure S3. The void volume available for infiltration(Φ) can be calculated using:

$$\phi(at\ RH = 22) = \phi(at\ RH = 0) - \theta(at\ RH = 22) \qquad (6)$$

These findings were also complemented by annealing a bilayer of Polystyrene-173K film atop SiO_2 NP packings for all the four sizes. Complete infiltration of polymers into the pores of the packings gave us another way to estimate the maximum void fraction inside the packing. The results have been shown in Figure S1.

Comment [DL]: Can you make this into a scatter plot like Figure 2?

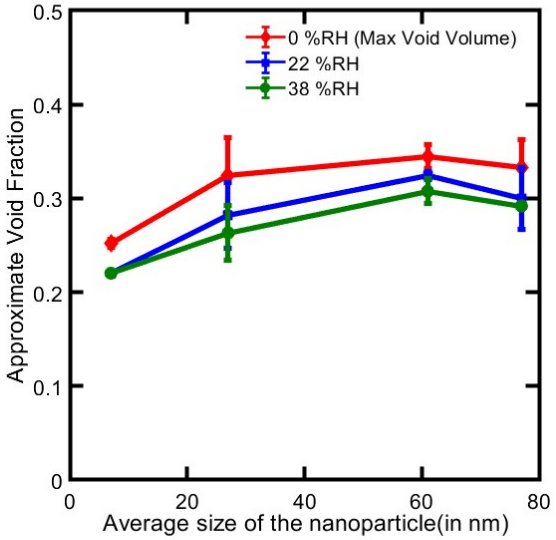

Figure S1. Approximate void fraction inside the packing at different humidity levels for particles of different sizes.

4. Kinetics of LeCaRI

The kinetics of the infiltration of oligomer chains into the NP voids is measured by maintaining contact between PDMS and NP films for different time periods on several different samples. The change in refractive index, measured using ellipsometry, is analyzed as explained in Section 1. The results are summarized in Figure S2. Negligible changes are observed after 5 sec, indicating that the infiltration of oligomers is completed within the first 5 seconds of LeCaRI.

The time required for the oligomers to infiltrate the packing can be estimated by assuming that LeCaRI follows the Lucas-Washburn model.

$$h^2 = \frac{\sigma R cos\theta}{2\tau^2\mu} t$$

(7)

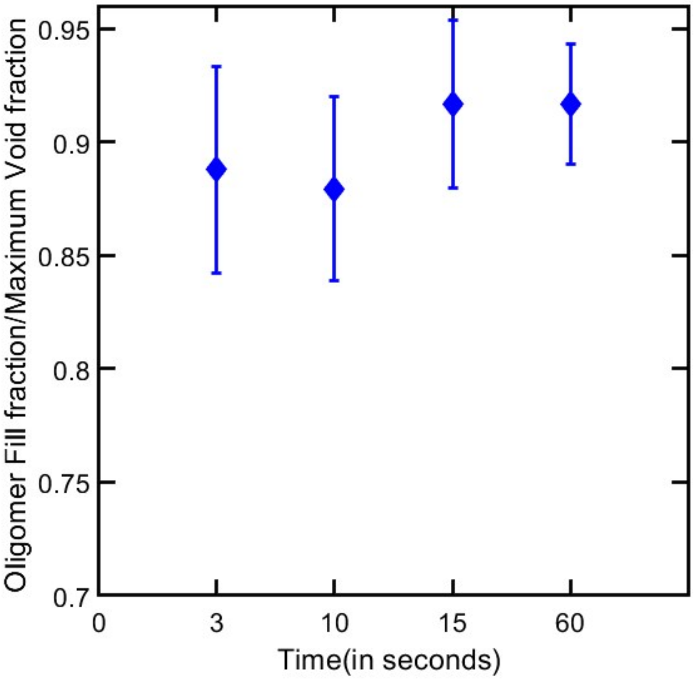

Figure S2.Amount of oligomer in packing versus the duration of LeCaRI.

where (describe the symbols). The viscosity of the base is specified as 4000 mPa.s after mixing at 23 ^{0}C.[6] The average radius of the pore is 30% of the radius of the particle close-packed in the NP film.[7] For TM50, this is $R = 0.3 \times 13.5 = 4.05\ nm$. PDMS has a surface tension value of 20 mN/m. The tortuosity of the packing is determined to be 1.95.[8] Assuming the wetting behavior of PDMS on silica to be such that cos(θ) ≈ 1, the time required for the oligomers to infiltrate the film of thickness h = 250 nm can be calculated as:

$$t = \frac{2h^2\mu\tau^2}{\sigma R cos\theta} = \text{ 0.0235 seconds} \ll 1 \text{ second.}$$

5. Patterning of PDMS surfaces and patterns observed using microscope

The photomasks for patterning PDMS are designed using AutoCAD 2018 and printed out from CAD/Art Service, Inc. (CA, USA). A positively embossed master mold is fabricated on a 3" silicon wafer using the conventional soft lithography technique in a cleanroom of Quattrone Nanofabrication Center of Singh Center of Nanotechnology at the University of Pennsylvania. Positive photoresist KMPR-1050 (MicroChem, MA, USA) is used and 100 micron thickness mold is fabricated with corresponding spin coat speed and UV exposure time. The master mold is subsequently silanized with Trichloro(1H,1H,2H,2H-perfluorooctyl)silane, PFOTS, to facilitate PDMS mold peel-off.

Polydimethylsiloxane (PDMS) precursor is prepared and cured as explained before. Once completely cured, the negatively embossed PDMS master is peeled off and surface-modified with oxygen plasma treatment, then left in vacuum with PFOTS for 2 hours. Another batch of degassed PDMS is then poured on PFOTS-coated PDMS master and cured for 4 hours at 65 ^{0}C. The upper PDMS slab with positively embossed features is peeled off and used as a stamp for patterning via LeCaRI. The NP films after LeCaRI using patterned PDMS are observed under an upright optical microscope in the reflection mode. The intensity of the images taken right after patterning are compared to the intensity of the image a month later to determine the loss in intensity of the pattern. This is done by calculating the local intensity in a rectangular region drawn on the image using ImageJ software's plot profile functionality. The intensity curves are normalized by dividing the intensity value at each point by the total intensity of pixels in the rectangle.

6. UV crosslinkable PDMS (UV-PDMS)

UV-PDMS KER-4690 is obtained from Shin-Etsu which comes as two components: Part A and Part B. Visible light can trigger the cross-linking catalyst once the two components are mixed, thus exposure to light is avoided as much as possible in all stages of the process. Part A and Part B are mixed in a 1:1 weight ratio in a plastic container wrapped with aluminium foil such that the total amount is 10 grams. Subsequently Sylgard 184 base and precursor are added to the plastic container in 10:1 ratio such that the total amount added is 5g. The weight ratios of UV-PDMS to PDMS are thus maintained at 2:1. The mixture is then degassed in a vaccum chamber for 30 minutes. The mixture is then poured onto a clean, cut silicon wafer in a petri dish and baked for 2 hours at 80 ^{0}C on a hot plate in a dark room. The cured PDMS gels are then cut into 1cm × 1cm square pieces and stored in a petri dish wrapped in aluminum foil until needed further.

The UV-PDMS+PDMS elastomer is brought into contact with a SiO_2 NP packing made from TM-50 SiO_2 NP (27 nm) such that one half of the top area of the film is patterned by LeCaRI. The front between the patterned and the un-patterned region is monitored by using an upright optical microscope in bright-field mode. ThorCam™ software is used for video acquisition by taking 1 frame every 2 minutes. The same is repeated for a region patterned using PDMS and a region patterned using UV-PDMS+PDMS. The latter is cured in a UV-ozone chamber for 20 minutes by exposure to UV(185 nm & 254 nm wavelength).

References

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