# SCALABLE AND VERSATILE FABRICATION OF OPAL STRUCTURES WITH SLOPE SELF-ASSEMBLY AND CAPILLARY PEELING FOR MICRODEVICES AND SENSORS

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## ABSTRACT

Self-assembly of opals has been extensively studied as a scalable bottom-up fabrication method capable of yielding ordered structures for applications such as optoelectronics, micro thermofluidic devices, and high power density electrodes. However, previous fabrication techniques are limited in the feature sizes achievable, require complex processes and equipment, or are limited in the substrates that can be used. In this work, we combine slope self-assembly with capillary peeling to overcome previous limitations. We demonstrate high-throughput fabrication of ordered opal structures, with a wide range of feature sizes and on previously unachievable substrates. Our experiments show that this approach can yield structures with over 90% crystallinity and that it is compatible with hydrophobic, rough, and curved substrates, therefore enabling new applications for opal structures.

## KEYWORDS

Self-assembly, opal, crystal, capillary peeling, transfer, optics, inverse opal, template

## INTRODUCTION

Opal structures, consisting of self-assembled, crystalline microsphere arrays, have been extensively studied as a material that due to its order can be used in a wide range of applications including sensing, micro electrochemical devices, lithography masks, optical coatings, and micro thermo-fluidics.[1]–[4] To satisfy the various requirements for these applications, multiple fabrication methods have been developed by leveraging the different types of attractive and repulsive interactions between colloidal particles. However, commonly used methods exhibited limited functionality or suffered from low scalability. For instance, previous methods such as vertical deposition and drop-casting were successful only over a narrow range of sphere sizes and on ultra-smooth, wetting surfaces, were very time-consuming, and suffered from significant crystalline defects.[1], [3], [5], [6]

Here, we demonstrate that by combining slope self-assembly (SSA) with capillary peeling and transfer of the opals we overcome these limitations. We show that this approach is compatible with sphere diameters ranging from 500 nm up to 10 μm. Through modeling, experiments, and image analysis, we develop and validate guidelines for the rational and fast fabrication of opals across this feature size range. Moreover, our method can be used to fabricate opals on previously challenging substrates such as hydrophobic, rough, and curved substrates. Interestingly, we observe that the crystallinity of the opal structures increases with transfer, with values exceeding 90% for opals transferred to the hydrophobic and rough substrates.

The flexibility and scalability of our approach can enable new applications as well as significant enhancement in the performance of applications using opals such as capillary-fed micro thermofluidic devices, micro battery electrodes, and optical sensors.[2], [4], [7]

## RESULTS

Figure 1 shows a schematic of our approach combining SSA with capillary peeling and transfer. First, we performed SSA, in which a colloidal solution of polystyrene microspheres suspended in 25% v/v ethanol and 75% v/v DI water was drop cast on an inclined glass slide which was rendered hydrophilic through plasma cleaning (Fig. 1a).[1] As the solvents evaporated, a monolayer array of close-packed spheres was achieved on smooth substrates with a high degree of hydrophilicity (contact angle ~0°). However, SSA on different substrates (e.g., surfaces with higher contact angles, rougher substrates such as mirror-polished copper) suffered from low order of the opal and from delamination of the opal from the substrate. To overcome these substrate-dependent challenges, we used capillary peeling to transfer the ordered opals from the glass slide to another desired substrate. The opal-covered glass slide was slowly dipped vertically into a water reservoir (Fig. 1b) causing the opal film to peel off from the substrate and float at the water-air interface while preserving its ordered shape. Finally, the suspended opal was transferred to a receiving substrate as the substrate was pulled upwards across the water-air interface (Fig 1c).

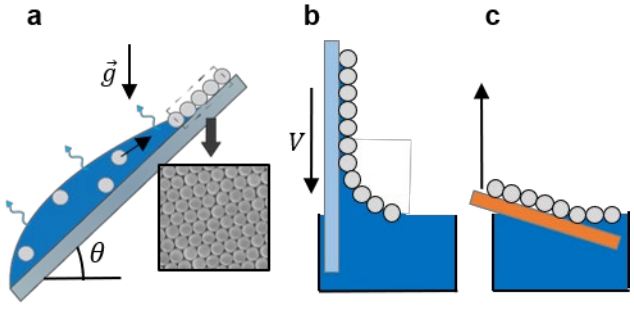


*Figure 1: Schematic of our fabrication process. a) An opal is formed through slope self-assembly in which a colloidal solution is drop cast on a hydrophilic glass slide and left to evaporate to the ambient. Capillary and evaporative forces lead to a close packed opal crystal. b) The opal is capillary peeled from the glass slide by dipping it at a slow speed V into a water reservoir. The opal is detached from the substrate and suspended on the water-air interface. c) The floating opal crystal is transferred to a receiving substrate as this substrate passes the water-air interface.*

To guide the opal fabrication process, in our previous work we modeled the self-assembly process (Fig. 1a) to extract guidelines for the use of SSA.[1] We demonstrated that for small spheres (diameter below 2 μm), the fraction of substrate that will be covered with spheres scales as

$$Coverage\ fraction \sim \left(\frac{\mu L \dot{m}''_{evap}}{\rho^2 g \sin\theta}\right)^{1/3} \frac{C}{(1-C)D} \qquad (1)$$

where $D$ is the diameter of the opal spheres and $C$, $\rho$, and $\mu$ are

the colloidal concentration, density, and viscosity of the solution, respectively. $\dot{m}''_{evap}$ is the evaporation rate flux, $L$ is the length of the substrate, $\theta$ is the inclination angle of the substrate, and $g$ is the gravitational acceleration.

We validated the scaling of Eq. 1 against experiments where we fabricated opals under different combinations of sphere diameters, temperatures, diameters, and inclination angles. We performed image analysis for these samples to extract the fraction of the substrate covered with opals and plotted it as a function of the parameter $\frac{C}{1-C}\frac{\sin\theta^{-1/3}}{D}$, as suggested by Eq. 1. Our results, shown in Fig. 2 for 500 nm and 2 μm diameter spheres, demonstrate that the opal coverage increases linearly with $\frac{C}{1-C}\frac{\sin\theta^{-1/3}}{D}$, as predicted by Eq. 1. We also observe that with higher temperatures, and therefore higher evaporation rates, this linear increase is faster, further validating our model. More importantly, our results show that the opal coverage can be tuned for the desired sphere size by choosing the appropriate temperature, angle, and concentration providing a path for the fast use of SSA.

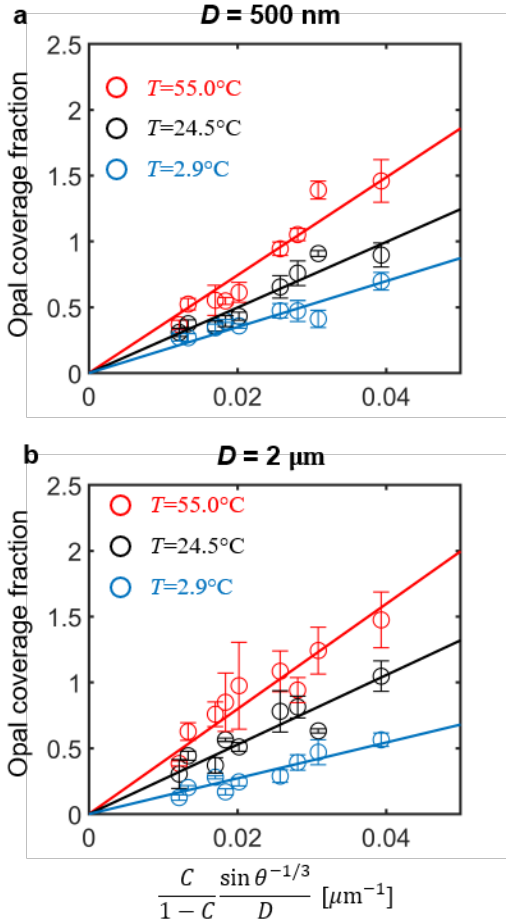


*Figure 2: Experimental and modeling results of opal coverage: Experimental results (circles) show the fraction of substrate covered with opals obtained from image processing for (a) 500 nm and (b) 2 μm spheres formed under different angles of inclination θ, temperatures of solvent, and colloidal concentrations C as a function of the parameter* $\frac{C}{1-C}\frac{(\sin\theta)^{-1/3}}{D}$*, obtained by our model. Values higher than 1 represent multilayer coverage. Solid lines correspond to the model results given by Eq. 1.*

For larger spheres of 10 μm diameter, capillary forces become more significant[8] and we observed that self-assembly is dominated by strong capillary interparticle attraction which causes spheres to self-assemble starting from the top of the substrate. As a result, assuming no sphere accumulation of spheres at the bottom of the substrate, the coverage fraction scales as

$$Coverage\ fraction \sim \frac{V_0 C}{D A_{sub}} \qquad (2)$$

where $V_0$ is the volume of solution drop-casted and $A_{sub}$ is the area of the substrate.

Following Eqs. 1 and 2, we were able to fabricate large-scale opal arrays with monolayer coverage for sphere sizes ranging between 500 nm up to 10 μm as shown in Fig. 3. As seen in Fig. 3, we were able to achieve ~1 $mm^2$ areas of monolayer coverage without a significant presence of double layers or voids. This method can also fabricate larger, centimeter-scale areas. However, these will exhibit small uncovered substrate areas or sphere stacking.

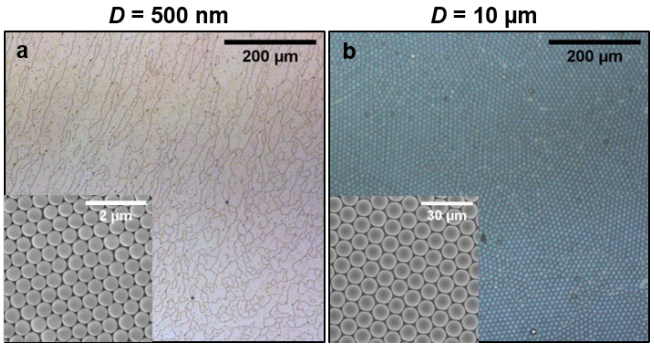


*Figure 3: Scanning electron microscopy (SEM) images of the 500 nm and 10 μm sphere samples. Samples were fabricated at room temperature, at a 45° angle, and with polystyrene concentrations of 3.4% v/v and 19.4% v/v, respectively. Opals obtained were ordered and polycrystalline and contained several defects, such as grain boundaries and vacancies.*

Our previous results show that slope self-assembly can generate opal structures in a scalable, high-throughput manner (~10 minutes per sample) and with a large range of spheres sizes. However, this method, as is the case for other commonly used colloidal self-assembly methods, is limited to highly wetting and smooth surfaces. This limitation severely restricts the applications where colloidal crystals can be used.

In order to enable the fabrication of opals in rough, nonwetting, and curved substrates, inspired by the capillary transfer of thin films at a liquid-air interface,[9] we capillary peeled the opals from the glass slide by dipping the slide vertically in a water bath at a slow speed (~1 mm/s). During capillary peeling, the spheres detach from the slide and float suspended in the air-water interface preserving their order, as seen in Figure 4. The floating opal can then be transferred to a receiving substrate as this substrate is passed slowly across the air-water interface.

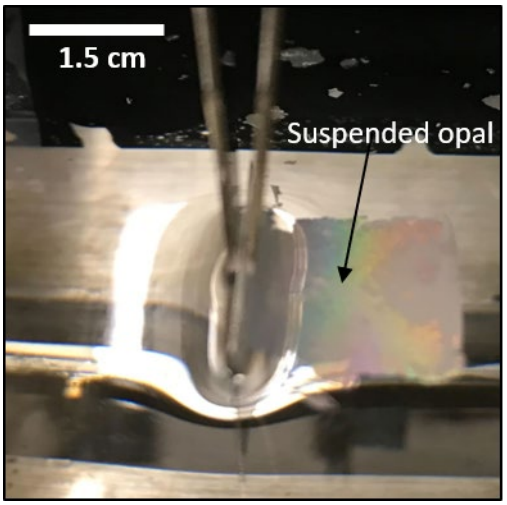


*Figure 4: Opal layer floating in the water-air interface after being peeled off from a glass slide. The opal maintains the square shape from the glass slide and the order, as indicated by the visible diffraction, during the capillary transfer process.*

This approach enabled transfer of opals to a wide variety of substrates while preserving the order of the sphere arrays. Fig. 5a shows a scanning electron microscope image (SEM) of 10 µm opals that were transferred to a silane coating glass with a contact angle of over 105° while Fig.5b shows an optical image of an opal that was transferred to the outer surface of a copper tube (shown in Fig. 5c). We additionally demonstrated transfer of the opal to the inside of a copper tube (Fig. 5d). We note that in spite of the hydrophobicity of the glass-coated slide and of the limited wetting, roughness, and curvature of the copper tube, the opal maintained good order as seen in Figs. 5a and 5b.

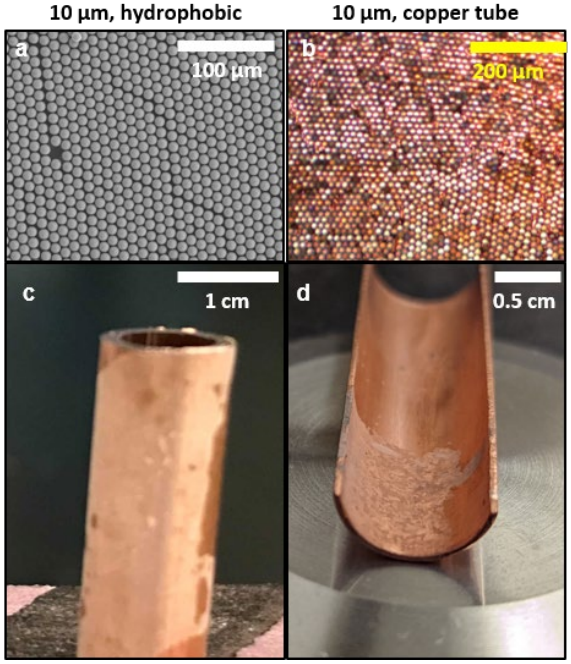


*Figure 5: Opals transferred to various substrates. a) Scanning electron microscopy (SEM) image of a 10 µm sphere sample transferred to a silane coated hydrophobic glass slide. b) Optical image of a 10 µm sphere sample transferred to the outside of a copper tube. c) Outside of the copper tube coated with opal structures. d) Inside of a copper tube coated with 10 µm opals.*

We further quantified the crystallinity of the opals fabricated with SSA on a glass slide and compared them with the crystallinity of opals transferred to a hydrophobic glass slide and to a mirror-polished flat copper piece. Specifically, we used a Voronoi diagram approach[10] to quantify using SEM images of opals the crystallinity of a sample at five different positions chosen randomly and we repeated this twice for the samples fabricated with SSA and three times for the transferred samples. Figure 6 shows the crystallinity results obtained, where each point corresponds to the average of all the values obtained for a given type of sample.

Our results show that the crystallinity of the samples fabricated on glass by SSA was about 85%, with minor variations as the sphere diameter changed. This value lies within the range of the crystallinity of samples fabricated via vertical deposition with spheres ranging from 100 nm up to 600 nm[10].

Interestingly, we observe that the transferred opals, which were originally fabricated on a glass slide via SSA and then transferred to the desired substrate, exhibit a higher degree of crystallinity than the opals fabricated only using SSA. The crystallinity of samples transferred to the hydrophobic glass and to the copper plate exceeded 90% with small differences across different sphere sizes and similar values regardless of the receiving substrate.

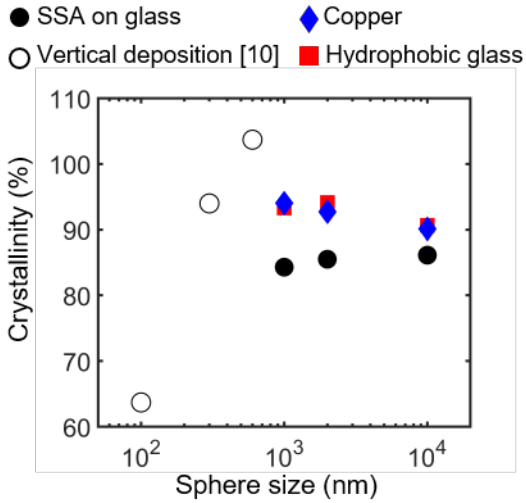


*Figure 6: Crystallinity of opals obtained through a Voronoi diagram approach. Vertical deposition yields opals with crystallinities ranging between 60% up to over 100%. In comparison, SSA yields opals with crystallinities of about 85%. Crystallinity increases during transfer reaching values above 90% for a copper substrate and for a hydrophobic glass slide.*

We hypothesize that the increase of crystallinity with transfer can be a consequence of forces acting during the transfer process. As the opal is peeled from the substrate the spheres push each other as they move away from the substrate leading to a densification of the opal. This is consistent with previous observations of how a similar transfer of opals can remove void spaces in opals with sub-monolayer coverage.[11] Additionally, the evaporation that accompanies the transfer to the receiving substrate can further enhance close-packing of spheres via capillary forces, leading to an increased crystalline order.

## CONCLUSIONS

In this work, we have demonstrated an approach for the fabrication of ordered opal structures in a scalable and high

throughput manner (<30 minutes/sample) over a large range of sphere sizes and on previously unachievable substrates. We investigated the different steps involved in our approach, developing guidelines for the rational and fast use of slope self-assembly for particles with diameters between 500 nm and 10 μm. We observed that our approach can be used to transfer ordered opals to rough, nonwetting, and curved substrates with crystallinities of over 90%, exceeding those of as-fabricated opals. This approach can enable the use of opals in a wide range of previously unattainable applications as well as enhance previously demonstrated performances for opal applications such as micro battery electrodes, optical sensors, and micro thermofluidic devices. Additionally, the insights from this approach can be used to reduce defects and enhance crystallinity of opals via a transfer approach.

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## CONTACT

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