

Fabrication of Large-Area Two-Dimensional Colloidal Crystals**

Jian-Tao Zhang, Luling Wang, Daniel N. Lamont, Sachin S. Velankar, and Sanford A. Asher*

Two-dimensional crystalline colloidal arrays (CCAs) have numerous applications, such as photonic crystal materials and sensors.^[1,2] Recently, numerous methods have been developed to prepare well-ordered 2D assemblies.^[3,4] These methods include spin coating,^[3a] dip coating,^[3b] and electrophoretic deposition^[3c] of colloidal particles on planar substrates to form 2D nanoparticle arrays. Particle assembly at interfaces can also be used to form 2D CCA monolayers.^[4] 2D particle arrays have previously been prepared on water surfaces.^[5] For example, Giersig and co-workers reported on the self-assembly of polystyrene (PS) latex particles on a water surface by applying a particle suspension to a clean silicon wafer, immersing the silicon wafer in water, and then consolidating the particle array by addition of surfactant. Through this method a few square centimeter 2D arrays were obtained.^[5a] Retsch et al. used a similar approach to prepare close-packed 2D colloidal crystals by floating and re-depositing colloidal monolayers at the air/water interface.^[5b] Qi and co-workers modified this approach by dropping an aqueous ethanol particle suspension onto a solid substrate that was surrounded by water.^[5c] The dispersion spread on the water surface, resulting in monolayer 2D films up to about 16 cm² in area.^[5c] Pan et al. developed a method to fabricate close-packed monolayer arrays of latex particles on a stirred water surface. Then they transferred the arrays onto a substrate.^[5e] The maximum sizes of the 2D array developed by the above methods appear limited to tens of square centimeters. There is a need to develop methods to prepare 2D arrays of larger sizes.

For example, Jeong et al. reported a method to form large-area 2D arrays based on a wire-wound rod coating method.^[6a] Recently, Vogel et al. presented a method to produce close-packed monolayers by using a glass slide to add colloid suspensions to the air–water interface. Close-packed monolayer patches crystallize upon spreading of an ethanolic PS colloid dispersion. Upon further addition of colloid, the patches eventually assemble into a monolayer covering the complete water surface.^[6b] Our group fabricated large 2D arrays by spreading alcohol/water solutions of colloidal particles on top of mercury surfaces.^[7] We obtained well-

ordered 2D arrays by self-assembly of colloidal particles on mercury as the solvent evaporated. These 2D arrays could easily be attached to hydrogel films.^[7] Although this method was very successful in preparing large-area 2D arrays, the use of mercury as a substrate is undesirable because of its toxicity.

Here, we report on fast fabrication of large 2D arrays of colloidal particles at the air/water interface by a needle tip flow method. The preparation of the 2D monolayer CCAs by this approach is illustrated in Figure 1 a. The tip of a sharpened

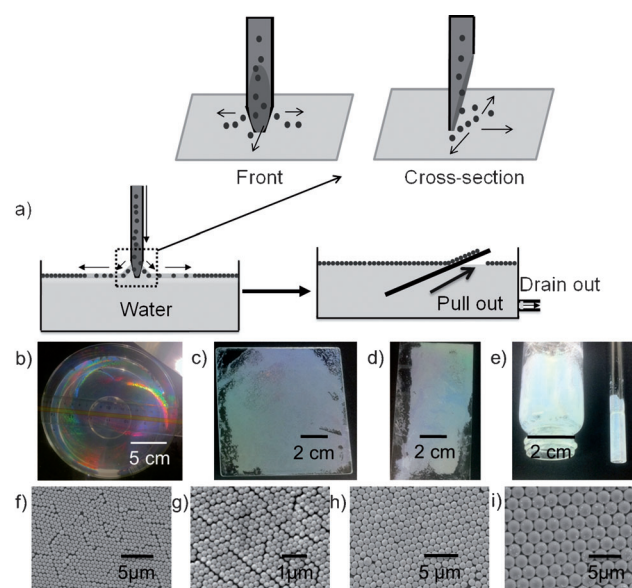


Figure 1. a) Fabrication of a 2D PS particle array by the needle tip flow technique. The transfer of the 2D arrays onto a substrate is shown by draining out the water or by lifting the array on a substrate. b) Photograph of 580 nm PS 2D array on the water surface in a glass dish 19 cm in diameter. 580 nm diameter PS 2D crystal arrays transferred onto c) flat glass, d) a plastic sheet, and e) a curved glass. SEM images of 2D arrays of f) 580 nm, g) 235 nm, h) 1 μm, and i) 2 μm PS particles.

injection needle was positioned to be just in contact with the water surface. The suspension was slowly and smoothly layered onto the top of the water surface to form monolayer particle arrays. The spreading force of the suspension drives the freshly formed particle array radially away from the needle tip to the outer edge of the dish. A beautiful continuous 2D array monolayer filled the entire water surface (> 280 cm² in the current study, Figure 1 b) in 2 min. The area of the resulting 2D arrays was as large as the area of the water surface used. Many 2D array applications will benefit from the ability to prepare large-area 2D arrays.

The spreading of the particle suspension uses the Marangoni effect in which a surface tension gradient causes the liquid surface to be pushed away from the regions of low

[*] Dr. J. T. Zhang, L. Wang, D. N. Lamont, Prof. S. A. Asher
Department of Chemistry, University of Pittsburgh
Pittsburgh, PA 15260 (USA)
E-mail: asher@pitt.edu

Prof. S. S. Velankar
Department of Chemical Engineering
University of Pittsburgh, Pittsburgh, PA 15261 (USA)

[**] S.A.A., J.-T.Z., and L.W. are grateful for the financial support from HDTRA (grant number 1-10-1-0044). This work was partially supported by funding from the NSF (grant number 0932901) and the AFOSR (Natural Materials and Systems & Extremeophiles Program award number FA 9550-10-1-0329).

surface tension. In the present case the Marangoni flow induced by adding the alcohol-containing colloidal dispersion onto the water surface causes the colloidal particle dispersion to rapidly spread outwards, thus covering the surface with particles.^[8]

The position of the needle tip is critically important for the formation of a 2D array on the water surface. The contact of the needle tip with the water surface forms a meniscus structure along the needle tip wall (Figure 1 a). This meniscus damps the vertical flow forces to prevent breaking of the water surface to enable the layering of the colloid dispersion on the water surface.

As shown in Figure 1 a we can transfer the floating 2D array onto a substrate by either draining the water and settling the 2D array on the substrate, or by lifting the substrate and depositing the 2D array on the substrate. Figure 1 c–e show examples of 580 nm diameter PS 2D crystal arrays transferred onto a flat glass slide, a flat plastic sheet, and curved glass substrates. Scanning electron microscopy (SEM) images show that the 2D arrays are hexagonally close-packed. The arrays form hexagonal multi-domains of areas larger than 20 μm^2 (Figure 1 f). Figure 1 g,h,i shows SEM images of 2D PS arrays with particle sizes ranging from 235 nm to 2 μm .

We conducted a quantitative analysis of the ordering of the 2D arrays shown in the SEM images (Figure 1) by calculating the 2D pair correlation function, $g(r)$ ^[9], given in Equation (1),

$$g(r) = \frac{1}{\langle \rho \rangle} \frac{dn(r, r+dr)}{da(r, r+dr)} \quad (1)$$

where a is the shell area and $n(r, r+dr)$ is the number of particles that lie within the shell considered. A SEM micrograph was first converted into a binary image, and then the MATLAB image processing toolbox was used to locate the centroid of each particle. The bulk particle density was calculated by dividing the total number of particles by the area of the polygon formed by the particles inside the edges of the image boundaries. The curves of $g(r)$ were calculated between $r = 0.05 R_0$ to $r = 30 R_0$ using shell thicknesses of $0.016 R_0$, where R_0 is the particle radius and r is the distance from the origin of the radial distribution function and $g(r)$ is the calculated distance. To properly accommodate particles near the boundaries, a sub-routine was used to determine the fraction of each $g(r)$ integration shell within the image boundaries.

As previously reported,^[9b,c] a quantitative measure of ordering is obtained from the ratio of the full width at half maximum (FWHM), κ , of the first peak in the Fourier transform of the function $g(r) - 1$ to that of a perfectly ordered array, κ_0 . The ratio of $\kappa/\kappa_0 = 1$ indicates a 2D colloidal crystal that is essentially perfect in 2D structural ordering, whereas $\kappa/\kappa_0 \leq 1.5$ suggests a very highly ordered 2D structure; $\kappa/\kappa_0 > 1.5$ indicates significant disordering.^[9b] Each SEM image was measured against a perfect array with comparable period, image resolution, and number of particles.

As shown in Figure 2 a, $g(r)$ shows a series of broad peaks that coincide with those calculated for a perfect array. The

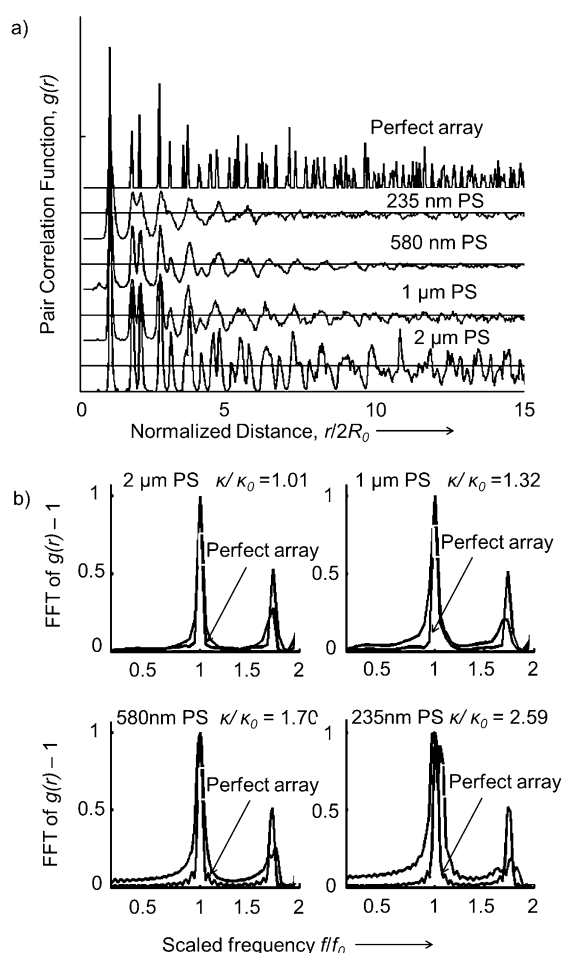


Figure 2. a) Curves of $g(r)$ calculated for 235 nm, 580 nm, 1 μm , and 2 μm PS particle arrays shown in Figure 1. Horizontal black lines indicate $g(r) = 1$. b) Single-sided power spectra Fourier transforms (FT) of $g(r)$ compared to FT of the corresponding perfectly ordered arrays. The power spectra were scaled to have identical maxima at $f/f_0 = 1$.

peak intensities of $g(r)$ decrease with the shell radius, $r/2 R_0$, which indicates that the 2D ordering decreases over long distances. The 2 and 1 μm PS arrays exhibit significant correlation beyond the tenth normalized distance, $r/2 R_0$. For the 235 nm PS array, the correlation is not evident for $r/2 R_0 > 5$. The κ/κ_0 values, calculated for 2 μm , 1 μm , 580 nm and 235 nm PS arrays, are 1.01, 1.32, 1.70, and 2.59, respectively (Figure 2 b), which indicates that the 2 μm PS array is nearly perfectly ordered, and the 1 μm array is highly ordered.

The ordering of 2D arrays decreases with the particle size. This is probably due to the fact that the thinner particle arrays are less robust. The ordering of the small size particle 2D arrays may have been disturbed by sample handling.

We modified our method to form 2D arrays on thin water films with the needle tip flow technique (Figure 3 a). After removing the water layer between the 2D array and the substrate, the 2D array can be easily transferred onto a substrate. Figure 3 b and c shows photographs of the 580 nm PS 2D arrays prepared on top of a glass and a plastic sheet. SEM images show that the arrangement of 2D particles was also hexagonally close-packed and consisted of multi-

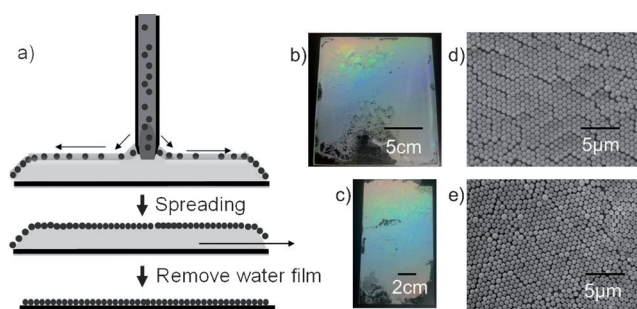


Figure 3. a) Fabrication of a 2D array on a flat substrate coated with a thin layer of water. Photographs of thus prepared 2D 580 nm PS arrays on b) a glass and c) a plastic sheet. SEM images of 580 nm PS 2D arrays on d) a glass and e) a plastic sheet.

domains (Figure 3 d and e), which are similar to the morphology of the 2D arrays prepared on bulk water and then transferred onto substrates (Figure 1 f).

Using this approach, we fabricated 2D array patterns that contained patches of particles of different sizes (Figure 4). We prepared a 490 nm PS 2D array patch first through the needle tip flow method (Figure 4 a) and then we used a dispersion of larger PS particles of 580 nm in diameter to form a patch with a larger spacing in the middle (Figure 4 b). These two particle arrays display different diffraction colors (Figure 4 d). We can imagine writing patterns of 2D arrays for particular applications in displays, for chemical separations, and sensing.

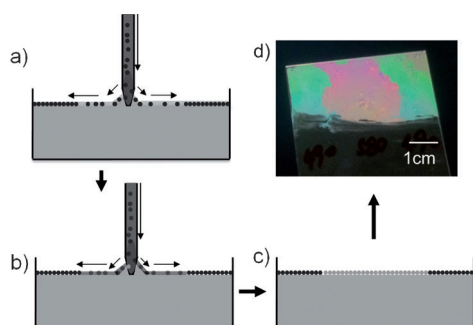


Figure 4. Fabrication of a 2D array pattern formed with patches of two different particle diameters. a) Spreading of a first particle array on water. b) Spreading of a second particle array. c) Resulting 2D array patterns on water. d) Visually observed diffraction of transferred 2D array pattern on a glass substrate.

Our 2D particle arrays on substrates can be further functionalized and used for sensing applications to visually detect analytes. As shown in Figure 5 a we fabricated a thin hydrogel film of 2D particles for pH sensing by depositing chitosan (CS, 2 wt %) that is dissolved in a 1 wt % acetic acid aqueous solution on a 2D particle array on a glass slide. We then evaporated the solvents, washed the CS film with a 0.4 M aqueous NaOH solution to neutralize the acid, and cross-linked the hydrogel in 0.5 wt % glutaraldehyde solution for 10 s. After washing with water, we obtained a pH-sensitive 2D PS array hydrogel film (Figure 5 b). Figure 5 c shows the SEM

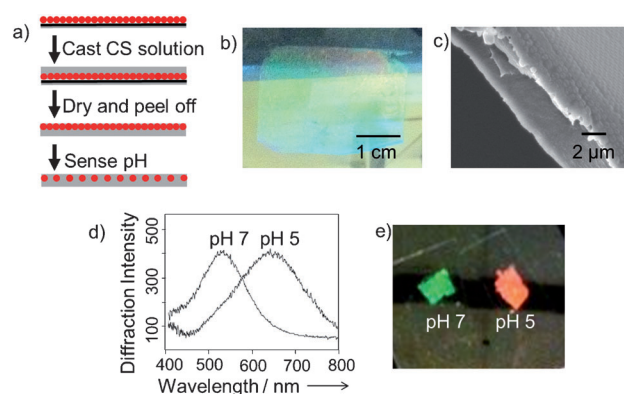


Figure 5. a) Preparation of a 2D array CS hydrogel film for pH sensing. The CS solution was poured on the 2D array on a glass slide, followed by drying in air. The 2D array CS hydrogel was peeled off the glass slide, washed with 0.4 M NaOH and water, and then cross-linked. The 2D array hydrogel sensed pH values by swelling and shifting the diffracted light wavelength. b) Photograph of a 2D array CS hydrogel in water. c) SEM image of a 2D array CS hydrogel film. d) Diffraction of a 2D array CS hydrogel film at pH 7 and 5. The measurement was carried out in a Littrow configuration with a measurement angle of about 32° between the probe and the normal to the 2D array. e) Photograph taken at an angle of 32° to the 2D array normal showing the 2D PS array CS hydrogel colors at pH 7 and 5. The 2D array hydrogels were placed on an Al mirror.

image of the 2D particles embedded in the dried CS hydrogel film.

We measured the diffraction in the Littrow configuration by using a six around one reflection probe where we excite with white light the surrounding six fibers and collect the diffracted light with the central fiber. The angle between the probe and the normal to the 2D array sensor was about 32°. Figure 5 d shows the diffraction spectrum of the 2D array CS films at pH 7 (in pure water) and at pH 5 (in 2-(*N*-morpholino)ethanesulfonic acid, MES buffer solution). At pH 7 diffraction is observed at 535 nm, whereas at pH 5 diffraction occurs at 645 nm. The CS hydrogel swells because of the protonation of its NH_2 groups at pH 5.^[10] The CS hydrogel film swelling increases the particle lattice spacing of the 2D array, which red-shifts the diffracted light. Figure 5 e shows a photograph of the 2D array CS hydrogel film sensors on a mirror surface that reflects the diffracted light.^[7a] The photograph clearly shows the green and red colors of the diffracted light.

In conclusion, we have developed a novel, simple, and efficient approach to rapidly fabricate large-area 2D particle arrays on water surfaces. These arrays can easily be transferred onto various substrates and functionalized for chemical sensing applications.

Experimental Section

Polystyrene (PS) particles with diameters of 490 and 580 nm were synthesized according to a previously reported method.^[11] The concentrations of 490 nm PS and 580 nm PS are 15 and 20 wt %, respectively, in water. The PS dispersion and propanol were mixed at a ratio of 2:1 in volume and the mixture was vortexed for 1 min. Then

the PS suspension was layered onto a water surface using a syringe pump (Razel A99-FM, Razel Scientific Instruments, Inc.). To transfer the 2D array onto a substrate, we lifted up the pre-placed substrate or drained the water in the container.

The arrangement and morphology of the array was observed by using a scanning electron microscope (SEM, Joel JSM6390LV) after sputter coating a thin layer of Au. Diffraction measurements were conducted at a fixed angle using an Ocean Optics USB2000-UV-VIS spectrometer, a LS-1 Tungsten Halogen Light Source and an R-series Fiber Optic Reflection Probe. The hydrogels were equilibrated in water (pH 7) or in MES buffer solution (pH 5) and then were put onto an Al glass mirror for diffraction measurements. The measurement was carried out in the Littrow configuration with a measurement angle of about 32° between the probe and the normal to the 2D array.

Received: August 2, 2011

Revised: April 18, 2012

Published online: May 8, 2012

Keywords: colloids · gels · nanoparticles · polymers · sensors

- [1] a) J. Zhang, Y. Li, X. Zhang, B. Yang, *Adv. Mater.* **2010**, *22*, 4249; b) Y. Xia, B. Gates, Y. Yin, Y. Lu, *Adv. Mater.* **2000**, *12*, 693; c) Y. Li, N. Koshizaki, W. Cai, *Coord. Chem. Rev.* **2011**, *255*, 357; d) S. M. Yang, S. G. Jang, D. G. Choi, S. Kim, H. K. Yu, *Small* **2006**, *2*, 458.
- [2] a) D. Xia, Z. Ku, S. C. Lee, S. R. J. Brueck, *Adv. Mater.* **2011**, *23*, 147; b) J. Zhang, B. Yang, *Adv. Funct. Mater.* **2010**, *20*, 3411; c) F. Li, D. P. Josephson, A. Stein, *Angew. Chem.* **2011**, *123*, 378; *Angew. Chem. Int. Ed.* **2011**, *50*, 360.
- [3] a) P. Jiang, M. J. McFarland, *J. Am. Chem. Soc.* **2004**, *126*, 13778; b) M. H. Kim, S. H. Im, O. O. Park, *Adv. Mater.* **2005**, *17*, 2501; c) R. Xie, X. Y. Liu, *Adv. Funct. Mater.* **2008**, *18*, 802.
- [4] a) C. Li, G. Hong, P. Wang, D. Yu, L. Qi, *Chem. Mater.* **2009**, *21*, 891; b) M. Yamaki, K. Matsubara, K. Nagayama, *Langmuir* **1993**, *9*, 3154; c) A. S. Dimitrov, C. D. Dushkin, H. Yoshimura, K. Nagayama, *Langmuir* **1994**, *10*, 432; d) M. Kondo, K. Shinozaki, L. Bergstroem, N. Mizutani, *Langmuir* **1995**, *11*, 394.
- [5] a) J. Rybczynski, U. Ebels, M. Giersig, *Colloids Surf. A* **2003**, *219*, 1; b) M. Retsch, Z. Zhou, S. Rivera, M. Kappl, X. S. Zhao, U. Jonas, Q. Li, *Macromol. Chem. Phys.* **2009**, *210*, 230; c) C. Li, G. Hong, L. Qi, *Chem. Mater.* **2010**, *22*, 476; d) J. Yu, Q. Yan, D. Shen, *ACS Appl. Mater. Interfaces* **2010**, *2*, 1922; e) F. Pan, J. Zhang, C. Cai, T. Wang, *Langmuir* **2006**, *22*, 7101.
- [6] a) S. Jeong, L. Hu, H. R. Lee, E. Garnett, J. W. Choi, Y. Cui, *Nano Lett.* **2010**, *10*, 2989; b) N. Vogel, S. Goerres, K. Landfester, C. K. Weiss, *Macromol. Chem. Phys.* **2011**, *212*, 1719.
- [7] a) J. T. Zhang, L. L. Wang, J. Luo, A. Tikhonov, N. Kornienko, S. A. Asher, *J. Am. Chem. Soc.* **2011**, *133*, 9152; b) J. T. Zhang, L. Wang, X. Chao, S. A. Asher, *Langmuir* **2011**, *27*, 15230.
- [8] a) L. E. Scriven, C. V. Sternling, *Nature* **1960**, *187*, 186; b) Y. Cai, B. M. Zhang Newby, *Appl. Phys. A* **2010**, *100*, 1221.
- [9] a) S. M. Allen, E. L. Thomas, *The Structure of Materials*, Wiley, New York, **1999**; b) R. Rengarajan, D. Mittleman, C. Rich, V. Colvin, *Phys. Rev. E* **2005**, *71*, 016615; c) J. J. Bohn, M. Ben-Moshe, A. Tikhonov, D. Qu, D. N. Lamont, S. A. Asher, *J. Colloid Interface Sci.* **2010**, *344*, 298.
- [10] E. Ruel-Gariépy, J. C. Leroux, *Polysaccharides for Drug Delivery and Pharmaceutical Applications*, American Chemical Society, New York, **2006**, chap. 12, p. 243.
- [11] C. Reese, S. A. Asher, *J. Colloid Interface Sci.* **2002**, *248*, 41.