

Vertical spreading of two-dimensional crystalline colloidal arrays†

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We report on a novel self-driven climbing of two-dimensional (2-D) ordered monolayer crystalline colloidal arrays (CCAs). This phenomenon can be used to rapidly and efficiently prepare large area, highly ordered 2-D array monolayer CCA films on various substrates. Large area 2-D polystyrene (PS) particle CCAs were fabricated on water surfaces by a needle tip flow technique. Introduction of a wet substrate through the 2-D particle monolayer array on the water surface causes the 2-D array to flow onto the wet substrate due to a surface spreading pressure. This method can quickly prepare ordered 2-D particle arrays on numerous wet substrates including flat/curved glass slides, inner walls of glass tubes, hydrogels, flexible polymer films, patterned surfaces, etc. By using responsive hydrogels as substrates, we can conveniently prepare 2-D photonic crystal sensors that can be used to visually determine analyte concentrations. For example, we prepared 580 nm PS 2-D arrays on poly(2-hydroxyethyl methacrylate) hydrogels to sense ethanol in water.

Self-assembled periodic crystalline colloidal arrays (CCAs) are of significant interest due to their important applications in photonic crystals, chemical sensors, and templates for fabrication of engineered meso/nano-structures.^{1–13} Two-dimensional (2-D) monolayer CCAs have been extensively studied and used for surface patterning and colloidal crystal templating.^{10–13} For example, hexagonally ordered triangular arrays and nanonets were fabricated by using 2-D colloidal crystal monolayers as masks.^{10,12} 2-D non-close packed polystyrene (PS) arrays were also prepared through reactive ion etching of close packed

PS 2-D arrays.¹³ All of these 2-D array applications require fast, efficient and inexpensive preparation methods.^{14,15}

Spin-coating, solvent evaporation and Langmuir–Blodgett deposition, *etc.* have been used to prepare 2-D colloidal arrays on planar rigid substrates.^{2,11} However, for some applications, it is necessary to prepare large area 2-D photonic crystals on flexible and soft substrates of complex geometries and properties, such as hydrogel surfaces and patterned surfaces. To date, no fast and facile methods have been reported to directly prepare well-ordered 2-D arrays, for example, on the inner walls of tubes or on swollen hydrogel films. For example, Zhang *et al.* reported a method to fabricate two-dimensional (2-D) negatively charged poly(styrene sulfate) colloidal crystals on a positively charged substrate. However, this strategy involves complex steps such as the three-dimensional (3-D) assembly of particles in ethanol and the electrostatic adsorption of these particles in water.¹⁴

We recently reported a method to prepare close packed PS 2-D arrays on mercury. These 2-D arrays can be transferred onto hydrogel thin films that change volume in response to targeted analytes.^{16,17} However, the toxicity of mercury limits the utilization of this approach. Instead, we developed methods to fabricate large area 2-D PS CCAs on water by spreading low surface tension PS aqueous alcohol suspensions onto water surfaces.¹⁸ 2-D array monolayers have been deposited on solid substrates by lifting the substrates through the water, capturing the floating 2-D arrays.^{19–24}

In an alternative method, Qi *et al.* developed a procedure for the self-assembly of large-area monolayer colloidal crystals at the air–water interface. In their method, a colloidal suspension was dropped on a glass slide that was placed in the center of a Petri dish with its edge at the same level as the surrounding water; the suspension spreads to self-assemble into a floating monolayer particle array that could be picked up by a substrate.²³ For practical applications, it is desirable to produce the 2-D array devices on complex substrates, such as on inside walls of tubes or on soft films having different chemistries and properties.

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† Electronic supplementary information (ESI) available: Movie showing the 2-D array flowing onto a wet substrate; photograph of a dry glass slide that is inserted through the 2-D array on a water surface shows no flow; illustration of the 2-D array preparation on an inclined wet substrate. See DOI: 10.1039/c2tc00794k

In this communication we report a method to coat 2-D colloidal PS array monolayer films onto complex substrates. We fabricated 2-D array monolayers on water surfaces in a 19 cm diameter glass dish by using our recently developed needle tip flow technique.¹⁸ We added propanol to the aqueous 20 wt% monodisperse 580 nm diameter PS dispersion (v/v 1 : 2) and spread the suspension on the water surface to assemble a monolayer 2-D PS particle array. The dispersion spreading and monolayer PS array formation rate on the water surface can be controlled by the pump injection speed and PS concentration. We prepared a wet glass slide by dropping water onto a hydrophilic Fisher precleaned microscope glass slide and tilting the slide to remove excess water. Then we inserted the wet glass slide through the water surface. The 580 nm PS 2-D array monolayer on the water surface immediately spreads to coat the wet substrate (Fig. 1a). As shown in the Movie (see ESI†), the 2-D array vertically climbs 6 cm within 25 s.

This 2-D array monolayer spreading is driven by a surface pressure that is caused by the surface tension difference between the water surface covered with the 2-D colloidal particle array layer and the water film on the wet substrate.²⁵ The higher surface tension of the water surface drives the spreading of the lower surface tension 2-D array water layer. Similar spreadings of nanoparticle films may have been observed previously.^{26–28}

We measured the room temperature surface tension by using a Fisher Surface Tensiomat (Model 21), which utilizes the Du Nouy ring method. We verified that ultrapure water has a surface tension of $72.8 \pm 0.7 \text{ mN m}^{-1}$, identical to the literature value (72.8 mN m^{-1});²⁹ in comparison, the surface tension of the PS 2-D array film on water is $70.3 \pm 2.3 \text{ mN m}^{-1}$. Therefore, as shown in Fig. 1c, inserting a wet substrate into the 2-D arrays results in a local surface tension difference between the 2-D array covered water surface and the bare water surface on the substrate. This surface pressure gradient forces the 2-D array to spread and cover the surface of the pre-wetted substrate.^{26–28}

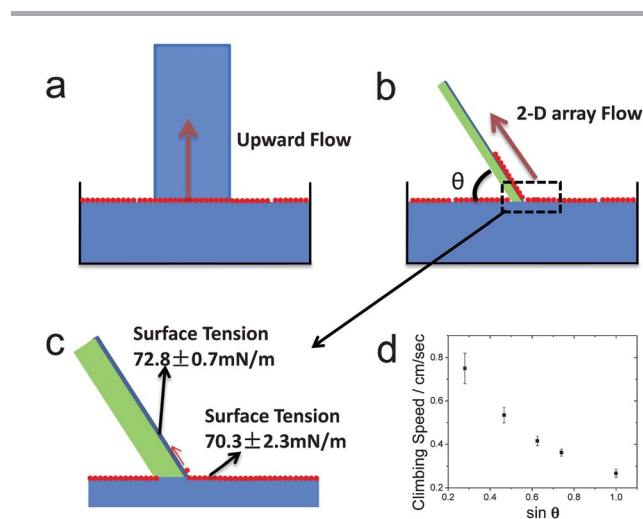


Fig. 1 (a and b) Illustration of flow of a 2-D CCA monolayer onto a wet substrate, (a) front view and (b) side view; (c) illustration of the surface pressure (Marangoni stress) that drives the 2-D arrays to flow from the water surface onto the wet substrate surface; (d) angle dependence of flow speed, where θ is the angle between the substrate and the water surface.

Fig. 1d shows the angular dependence of the flow velocity of the 2-D CCA, where θ is the glancing angle between the substrate and the 2-D array on the water surface. The 2-D array climbs slowest at normal incidence ($\theta = 90^\circ$). The flow rate increases as the glass substrate is tilted to smaller θ values. We expect that the spreading speed, v is controlled by the viscous forces, the difference in surface tension and gravity: $v = (\text{Marangoni stress} - \text{gravity})/\text{viscosity}$. As the film is tilted, the effective gravitational force is reduced, allowing faster spreading. Thus, we can control the climbing rate by tilting the wet substrate.

The thickness of the water film on the wet substrates ranges from 50 to 100 μm , which is much thicker than the thickness of the 2-D monolayer particle array (580 nm). If the water film is thin (for example, less than 5 μm), the water evaporates before significant 2-D film climbing occurs, which stops the spreading because 2-D arrays do not flow on dry surfaces. If a dry slide is inserted into the 2-D array on the water surface, the 2-D film does not climb (ESI Fig. S1†). This result is consistent with previous studies of particles on oil/water surfaces that showed that the surface pressure of particle-laden films is not adequate to overcome contact line pinning on dry surfaces.²⁷ Prewetting the surface enables spreading by providing a mobile layer on which the particles can spread due to the small surface pressure driving forces.

In the previously reported method, floating 2-D arrays were transferred onto a substrate by draining the water and settling the 2-D arrays onto the substrate, or by lifting the pre-placed substrate and depositing the 2-D arrays on it.¹⁸ This existing method does not coat 2-D arrays onto complex surfaces, such as on the inner walls of tubes where only the outer surfaces contact the 2-D arrays. Our new self-climbing technique has important advantages compared to previously reported 2-D array preparation methods. For example, the 2-D array self-assembles and coats complex surfaces. Essentially all wet substrate surfaces can be coated with this approach. Fig. 2a shows a photograph of a 2-D photonic crystal array of 580 nm diameter PS spheres on the surface of a flat glass slide. The color gradient in Fig. 2a is caused by the variation of incidence angle of the light to the 2-D array across the sample surface because we used a diverging light source. According to the 2-D diffraction theory formula for the Littrow configuration:¹⁶ $m\lambda = 3^{1/2} d \sin \theta$, where m is the diffraction order, λ is the diffracted wavelength (in vacuum), d is the 2-D particle spacing, and θ is the incidence angle of the light relative to the 2-D array normal, the diffraction wavelength red-shifts with increasing θ . In Fig. 2a, the incidence angle, θ , increases from the left bottom to the right top of the glass substrate, therefore the diffraction color observed changes from blue to green, yellow and red.

Fig. 2b shows that the 2-D array has a hexagonal ordering and consists of multidomains with domain sizes $>20 \mu\text{m}^2$. We observed the 2-D arrays from different areas of the glass substrates by SEM. The particles are hexagonally close packed and therefore the packing density is constant. We did not find multi-layers. Fig. 2c shows the 2-D photonic crystals spread onto the inner wall of a glass tube.

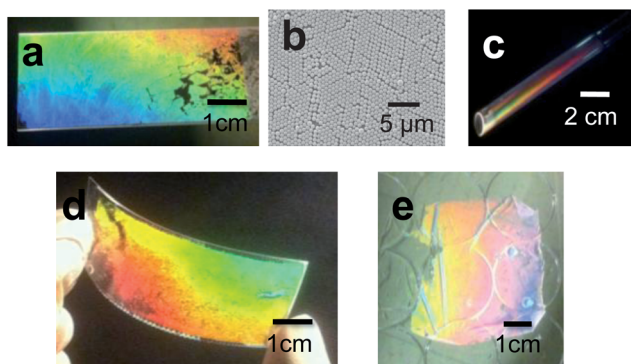


Fig. 2 (a) Photograph of a dried 580 nm diameter PS 2-D array on a glass slide; (b) SEM image of a 580 nm PS 2-D array on a flat glass slide; photographs of 580 nm diameter PS 2-D arrays (c) inside a glass tube, (d) on a PAAm hydrogel and (e) on a chitosan hydrogel film. We used diverging light and took the photographs in a forward diffraction direction. In this situation, the incidence angle of the light to the normal of the 2-D array varies across the samples, causing the observed diffraction wavelength color gradient. The PAAm hydrogel was formed on top of a polyacrylamide gel support film (2.4 cm × 6 cm, Biorad) by polymerization of 0.5 mL of a solution of acrylamide (10 wt% in water) and *N,N'*-methylenebisacrylamide (0.2 wt% in water). The chitosan film was fabricated by evaporation of 15 mL chitosan (CS, 2 wt%) solution dissolved in a 1 wt% acetic acid aqueous solution in a 10 cm diameter plastic dish. The dried film was washed with 0.4 M aqueous NaOH solution to neutralize the acid and then with water to remove impurities. The 2-D arrays were coated onto the PAAm hydrogel and the CS film by inserting these wet hydrogel films through the 2-D array water surfaces.

Our preparation method for 2-D array particle monolayers on substrates is much faster than previously reported methods. Although solvent evaporation induced self-assembly and electrostatic self-assembly can form 2-D particle monolayers on inside walls of containers,¹⁴ these methods are very slow (hours or days) and the experimental conditions, such as the evaporation rate, the concentration of particles, *etc.*, must be very carefully controlled. Here the climbing of a 2-D array onto a wet glass slide (Fig. 2a, 1 × 3 inches) only takes ~20 to 25 s and no control of conditions, other than substrate wetting, is necessary.

The preparation of 2-D arrays can be further simplified by contacting the wet substrate with the water surface prior to assembling of the 2-D array by using the needle tip flow method,¹⁸ as shown in the ESI, Fig. S2.† The water film on the inclined substrate extends the water surface for particle array spreading and array self-assembly. Monolayer 2-D array CCAs form not only on the water surface but also on the thin water film substrate surface. The 2-D array adheres to the substrate on drying.

We can also attach the 2-D array onto any substrate coated by a water film. Fig. 2d and e show the 2-D arrays on a polyacrylamide (PAAm) hydrogel covalently polymerized onto a plastic film and onto a chitosan hydrogel film attached to a plastic sheet. These 2-D photonic crystal array hydrogels exhibit strong diffraction when placed on a mirror. This enables these photonic crystal-hydrogels to be used for the visual determination of analytes.^{16,18}

Our new method can coat 2-D arrays showing strong 2-D diffraction onto responsive hydrogels. This climbing approach

facilitates the development of 2-D array hydrogel sensors. We prepared a 2-D hydrogel sensor by synthesizing a thin poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogel film by photo-polymerization. We used the technique discussed above to flow the 580 nm PS 2-D array onto the PHEMA hydrogel. The 2-D array PHEMA hydrogel was then dried in air which caused adhesion of the 2-D particle array. The hydrogel was then re-swelled in water.

Fig. 3a and b show the SEM images of air dried 2-D arrays on the PHEMA hydrogel. The 2-D arrays are hexagonally ordered. The 2-D particles adhere to the PHEMA hydrogel surface, as shown in the SEM image taken at a tilt angle of 45° (Fig. 3b).

Fig. 3c and d show that the diffraction of the 2-D array PHEMA sensor equilibrates in different ethanol–water solutions red-shifts as the ethanol concentration increases. This occurs because of the increased favorability of mixing associated with the decreased Flory–Huggins mixing parameter.³⁰ The swelling of the PHEMA hydrogel increases the 2-D array particle spacing, *d*.^{17,30} The increase in *d* with increasing ethanol concentration red-shifts the diffracted wavelength.

We also prepared 2-D photonic crystals with multiple particle diameter arrays by placing a wet substrate into different particle diameter 2-D colloidal crystal arrays on water surfaces. For example, Fig. 4a shows 2-D arrays of both 490 nm and 580 nm diameter PS particles prepared by successively placing the substrate into the 490 and 580 PS 2-D array films. The first array monolayer is coated onto the slide. The second array monolayer shifts the first 2-D array on the wet substrate as it subsequently climbs onto the substrate. This process can be repeated to place different diameter particle arrays onto the substrate.

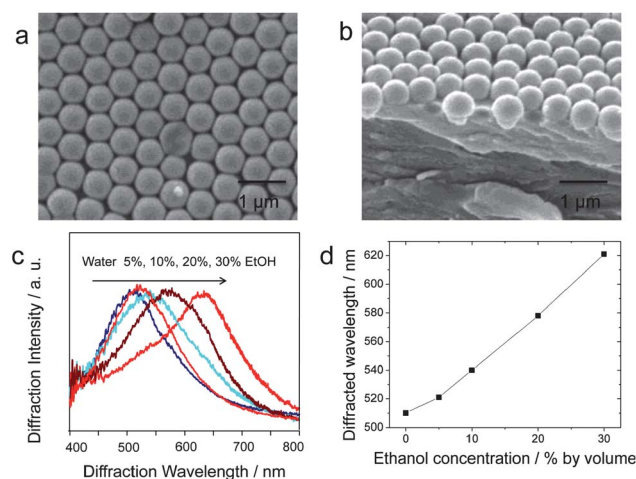


Fig. 3 (a) and (b) SEM images of a 580 nm diameter PS array on a PHEMA hydrogel film at normal (a) and at a tilt angle of 45° (b); (c) normalized diffraction spectra of 2-D PHEMA hydrogels equilibrated in ethanol–water solutions ranging from 0 to 30% by volume. Diffraction measurements utilized an Ocean Optics USB2000-UV-VIS Spectrometer, a LS-1 Tungsten Halogen Light Source and an R-series Fiber Optic Reflection Probe in a Littrow configuration. The measurement angle between the probe and the normal to the 2-D array is 31°; all diffraction measurements were obtained from the 2-D array hydrogels placed on a front surface silver mirror. (d) Diffraction wavelength versus ethanol concentration.

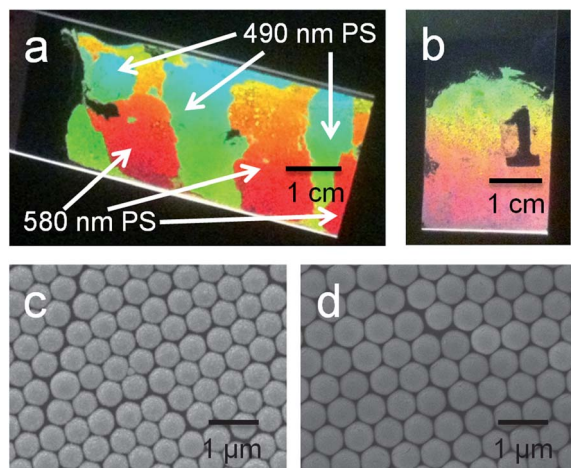


Fig. 4 (a) Photograph of different 2-D array patterns on a single substrate. The patterns consist of 580 nm and 490 nm PS particle arrays. The photograph was taken with diverging white light in the forward scattering geometry; (b) 2-D CCA formed on a patterned surface. The position of the number "1" is coated with Sigmacote and is highly hydrophobic. No water thin film forms on this area. Thus, this area is not coated by the particle arrays; (c and d) SEM images of 490 and 580 nm diameter PS arrays shown in (a).

The diffraction wavelength, λ , is proportional to the 2-D array particle spacing, d .^{16,31} The color difference in Fig. 4a is caused by the difference in particle spacings. A larger particle spacing results in a longer diffraction wavelength. Therefore, the 580 nm diameter 2-D arrays show a red to orange diffraction color while the 490 nm diameter 2-D arrays show a green to blue diffraction color (Fig. 4a). Fig. 4c and d show the SEM images of the 490 and 580 nm diameter PS arrays shown in Fig. 4a. We controlled the diffraction wavelength by changing the diameter of the particles used for the 2-D array.

We can also prepare specific 2-D array patterns by controlling the substrate wetting. We painted the number "1" on a frosted glass slide with a Sigmacote hydrophobic coating. After heating, the coated area is highly hydrophobic. Fig. 4b shows the image of the number "1" whose area excluded the flowing 2-D particles array.

In conclusion, we describe a method to prepare 2-D CCAs on substrates with complex geometries and surface chemistries. We utilized a surface tension difference to force 2-D arrays on water to spread onto wet substrate surfaces. We used this approach to prepare 2-D PCCA PHEMA hydrogel photonic crystal sensors for the visual detection of ethanol.

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Notes and references

1 M. E. Stewart, C. R. Anderton, L. B. Thompson, J. Maria, S. K. Gray, J. A. Rogers and R. G. Nuzzo, *Chem. Rev.*, 2008, **108**, 494.

- 2 Y. Xia, B. Gates, Y. Yin and Y. Lu, *Adv. Mater.*, 2000, **12**, 693; J. Ge and Y. Yin, *Angew. Chem., Int. Ed.*, 2011, **50**, 1492.
- 3 F. Li, D. P. Josephson and A. Stein, *Angew. Chem., Int. Ed.*, 2011, **50**, 360.
- 4 E. C. Nelson, N. L. Dias, K. P. Bassett, S. N. Dunham, V. Verma, M. Miyake, P. Wiltzius, J. A. Rogers, J. J. Coleman, X. Li and P. V. Braun, *Nat. Mater.*, 2011, **10**, 676.
- 5 J. M. Weissman, H. B. Sunkara, A. S. Tse and S. A. Asher, *Science*, 1996, **274**, 959.
- 6 Z. Hu, X. Lu and J. Gao, *Adv. Mater.*, 2001, **13**, 1708.
- 7 Y. Takeoka and M. Watanabe, *Adv. Mater.*, 2003, **15**, 199.
- 8 J. G. McGrath, R. D. Bock, J. M. Cathcart and L. A. Lyon, *Chem. Mater.*, 2007, **19**, 1584.
- 9 J. R. Lawrence, G. H. Shim, P. Jiang, M. G. Han, Y. Ying and S. H. Foulger, *Adv. Mater.*, 2005, **17**, 2344.
- 10 C. L. Haynes and R. P. Van Duyne, *J. Phys. Chem. B*, 2001, **105**, 5599.
- 11 J. Zhang, Y. Li, X. Zhang and B. Yang, *Adv. Mater.*, 2010, **22**, 4249; S. Yang and Y. Lei, *Nanoscale*, 2011, **3**, 2768; X. Ye and L. Qi, *Nano Today*, 2011, **6**, 608.
- 12 C. Li, G. Hong and L. Qi, *Chem. Mater.*, 2010, **22**, 476.
- 13 B. J. Y. Tan, C. H. Sow, K. Y. Lim, F. C. Cheong, G. L. Chong, A. T. S. Wee and C. K. J. Ong, *J. Phys. Chem. B*, 2004, **108**, 18575.
- 14 X. Zhang, J. Zhang, D. Zhu, X. Li, X. Zhang, T. Wang and B. Yang, *Langmuir*, 2010, **26**, 17936.
- 15 G. A. Ozin and S. M. Yang, *Adv. Mater.*, 2001, **11**, 95.
- 16 J. T. Zhang, L. Wang, J. Luo, A. Tikhonov, N. Kornienko and S. A. Asher, *J. Am. Chem. Soc.*, 2011, **133**, 9152; J. T. Zhang, N. Smith and S. A. Asher, *Anal. Chem.*, 2012, **84**, 6416.
- 17 J. T. Zhang, L. Wang, X. Chao and S. A. Asher, *Langmuir*, 2011, **27**, 15230.
- 18 J. T. Zhang, L. Wang and S. A. Asher, *Angew. Chem., Int. Ed.*, 2012, **51**, 6117.
- 19 J. Rybczynski, U. Ebels and M. Giersig, *Colloids Surf., A*, 2003, **219**, 1.
- 20 M. Retsch, Z. Zhou, S. Rivera, M. Kappl, X. S. Zhao, U. Jonas and Q. Li, *Macromol. Chem. Phys.*, 2009, **210**, 230.
- 21 F. Pan, J. Zhang, C. Cai and T. Wang, *Langmuir*, 2006, **22**, 7101.
- 22 N. R. Thomson, M. A. McLachlan, C. L. Bower and D. W. McComb, *Langmuir*, 2009, **25**, 11344.
- 23 C. Li, G. Hong, P. Wang, D. Yu and L. Qi, *Chem. Mater.*, 2009, **21**, 891.
- 24 P. Masse and S. Ravaine, *Colloids Surf., A*, 2005, **270**, 148.
- 25 L. E. Scriven and C. V. Sterling, *Nature*, 1960, **187**, 186.
- 26 H. L. Cheng and S. S. Velankar, *Colloids Surf., A*, 2008, **315**, 275.
- 27 K. S. Mayya and M. Sastry, *Langmuir*, 1999, **15**, 1902.
- 28 B. P. Binks, J. H. Clint, P. D. I. Fletcher, T. J. G. Lees and P. Taylor, *Langmuir*, 2006, **22**, 4100.
- 29 L. Y. Zhang, S. Lawrence, Z. Xu and J. H. Masliyah, *J. Colloid Interface Sci.*, 2003, **264**, 128.
- 30 X. Xu, A. V. Goponenko and S. A. Asher, *J. Am. Chem. Soc.*, 2008, **130**, 3113.
- 31 A. Tikhonov, N. Kornienko, J. T. Zhang, L. Wang and S. A. Asher, *J. Nanophotonics*, 2012, **6**, 063509.