



In-Plane Direct-Write Assembly of Iridescent Colloidal Crystals

Alvin T. L. Tan, Sara Nagelberg, Elizabeth Chang-Davidson, Joel Tan, Joel K. W. Yang, Mathias Kolle, and A. John Hart*

Materials made by directed self-assembly of colloids can exhibit a rich spectrum of optical phenomena, including photonic bandgaps, coherent scattering, collective plasmonic resonance, and wave guiding. The assembly of colloidal particles with spatial selectivity is critical for studying these phenomena and for practical device fabrication. While there are well-established techniques for patterning colloidal crystals, these often require multiple steps including the fabrication of a physical template for masking, etching, stamping, or directing dewetting. Here, the direct-writing of colloidal suspensions is presented as a technique for fabrication of iridescent colloidal crystals in arbitrary 2D patterns. Leveraging the principles of convective assembly, the process can be optimized for high writing speeds ($\approx 600 \mu\text{m s}^{-1}$) at mild process temperature (30 °C) while maintaining long-range (cm-scale) order in the colloidal crystals. The crystals exhibit structural color by grating diffraction, and analysis of diffraction allows particle size, relative grain size, and grain orientation to be deduced. The effect of write trajectory on particle ordering is discussed and insights for developing 3D printing techniques for colloidal crystals via layer-wise printing and sintering are provided.

Nature is replete with instances of hierarchically structured materials that create visually stunning appearances. For example, peacock feathers, butterfly wings, and beetle shells are structured on the nano-, meso-, and macroscales, resulting in iridescence and structural color.^[1–3] There is also much scientific interest and commercial value in creating similarly structured man-made materials for applications including photonic devices and visual displays.

These and other technology needs require materials fabrication techniques that provide control of material structure over

multiple length scales. Self-assembly provides a convenient means for controlling material structure from the bottom up, and there has been substantial research on convective self-assembly of colloidal particles into photonic crystals, including seminal work by Vlasov^[4] and others.^[5–8] Patterned colloidal crystals have been created for photonic devices and sensing applications.^[9–11] However, these techniques often require the prefabrication of templates or masks, and lithographic etching,^[6,12] especially when spatial control of the material is required. An alternate approach would be to print colloidal particles directly onto the substrate from a digital template so that steps such as template fabrication, masking, and etching, can be omitted. Printing from a digital template can be done with inkjet printing, where droplets 20–50 μm in diameter are ejected on-demand from microscopic nozzles.^[13–16] However, the size of the droplet

limits the grain sizes in the resulting colloidal crystal, resulting in weak structural color.^[17] Moreover, most inkjet printing techniques require colloidal particle sizes to be limited from 50 to 300 nm for smooth printing,^[16,18] and printing larger particles presents nozzle clogging issues.

The combination of direct-write 3D printing with the principle of self-assembly is a potential means to create new hierarchically-ordered materials. For instance, by dispensing a colloidal solution onto a temperature-controlled substrate and coordinating the rate of crystal growth with the retraction of the substrate, it is possible to fabricate colloidal crystals into specific shapes, such as vertical pillars and helices.^[19] Here, we extend this technique to the more general case of planar direct-write self-assembly, where evaporation-induced assembly of colloidal particles is guided by the moving meniscus traced by a motorized, liquid-dispensing needle. We show that direct-write self-assembly can build high-quality iridescent colloidal crystals in arbitrary patterns predetermined by a digital template.

Direct-write assembly is performed by the scheme shown in **Figure 1a**. A substrate, typically a piece of silicon wafer or glass, is mounted onto a temperature-controlled (30 °C) precision motion stage with a dispensing needle positioned slightly above the substrate. An aqueous suspension of polystyrene particles (diameter $D = 746 \text{ nm}$) is dispensed through the needle and contacts the substrate, forming a liquid meniscus between the needle and the substrate. Unlike slurry inks used in direct ink writing,^[20,21] the concentration of the particles is low, and

A. T. L. Tan
Department of Materials Science and Engineering
Massachusetts Institute of Technology
77 Massachusetts Ave, Cambridge, MA 02139, USA

S. Nagelberg, E. Chang-Davidson, Prof. M. Kolle, Prof. A. J. Hart
Department of Mechanical Engineering
Massachusetts Institute of Technology
77 Massachusetts Ave, Cambridge, MA 02139, USA
E-mail: ajhart@mit.edu

J. Tan, Prof. J. K. W. Yang
Pillar of Engineering Product Development
Singapore University of Technology and Design
8 Somapah Road, Singapore 487372, Singapore

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/smll.201905519>.

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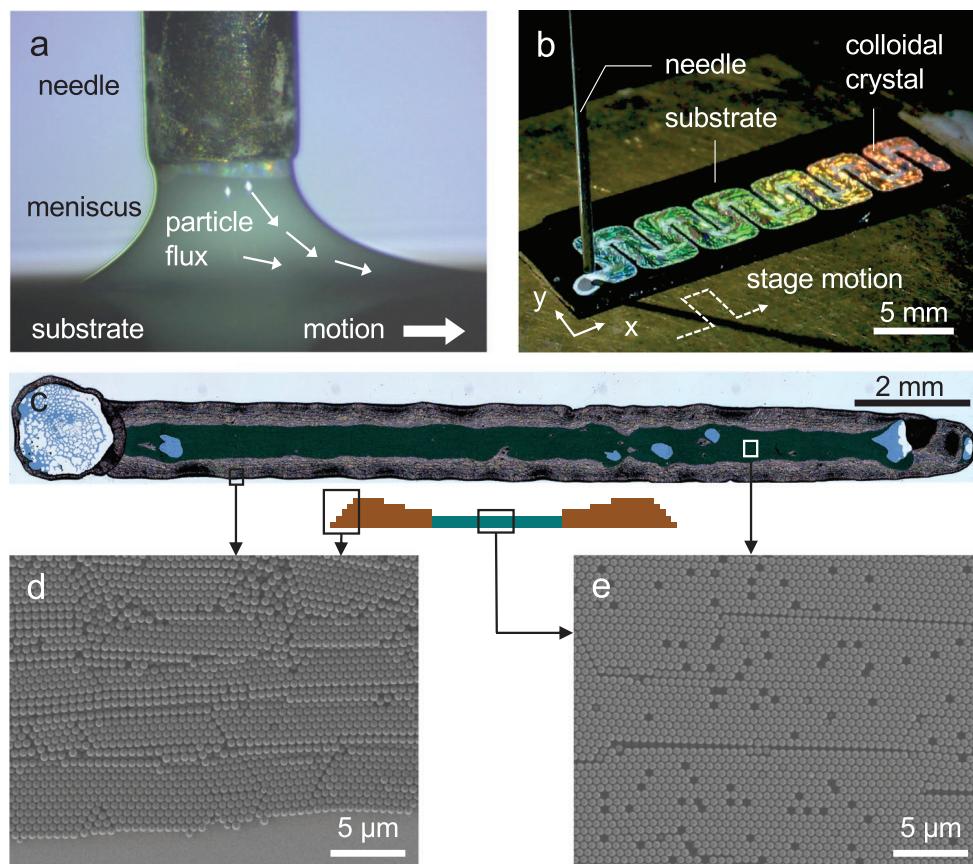


Figure 1. Fabrication of colloidal crystals by in-plane direct-write self-assembly. a) In-plane direct-write self-assembly is performed by precision dispense of a colloidal suspension from a needle, coupled with lateral substrate motion. b) A serpentine colloidal crystal is drawn by movement of the stage. c) Optical image (top) and cross-section schematic (bottom) of an exemplary colloidal crystal trace. The edge of the crystal (brown coloration) is thicker than the middle. The middle consists of mostly particle bilayers (green coloration) and monolayers (blue coloration). d) SEM image showing multilayer terraces at the edge of the crystal. e) SEM image of the middle region of the crystal showing defects such as dislocations and vacancies.

therefore the flow properties of the suspension is similar to the solvent (i.e., water). The substrate is then moved laterally by the stage, while maintaining the gap between the substrate and the needle. As the substrate moves, particles are transported to the trailing edge of the meniscus by an evaporation-induced flux. The particles are then compacted into a colloidal crystal at the trailing edge of the meniscus. Therefore, a crystal can be written by relative motion of the needle over the stage at a velocity matching the approximate rate of crystal growth. An optical image of an exemplary colloidal crystal is shown in Figure 1c. By this method, the trajectory of crystal growth can be influenced by multiaxial stage motion. As an example, Figure 1b shows a serpentine-shaped crystal which appears iridescent to the naked eye, made by coordinated in-plane motion of the stage beneath the needle.

For the purpose of studying the rate of crystal growth, we move the stage in a single direction at a constant speed, denoted as the write speed. The layer thickness of the colloidal crystal can be identified by its thin film interference colors.^[22,23] In Figure 1c, blue regions correspond to particle monolayers, green regions correspond to bilayers, and the brown regions correspond to three or more layers of particles. We observe that the edge of the crystal is thicker than the middle, a result of outward capillary flow toward the contact line of the meniscus.

However, the thickness of the middle region is uniform and can be controlled by the write speed, as will be discussed in detail later. Scanning electron microscopy (SEM) imaging confirms the presence of multiple layers of particles at the edge (Figure 1d) and a uniform crystal thickness in the middle region. In the middle region, the particles are hexagonally packed, albeit with typical crystal defects such as vacancies and dislocations.

The key to continuous direct-write self-assembly of colloidal crystals is matching the write speed to the rate of crystal growth determined by evaporative flux from the trailing meniscus. We can approximate the rate of crystal growth at the trailing end of the meniscus to be that of other convective assembly techniques such as dip-coating and blade-casting. By considering the balance of the rate of crystal growth with the flux of water and particles transported to the crystal growth front, Dimitrov and Nagayama^[24] proposed the following equation to calculate the rate of crystal growth v_c

$$v_c = \frac{\beta l_j \varphi}{h(1-\varepsilon)(1-\varphi)} \quad (1)$$

Here, h is the height of the crystal, ε its porosity, and φ is the volume fraction of particles in suspension, as depicted in

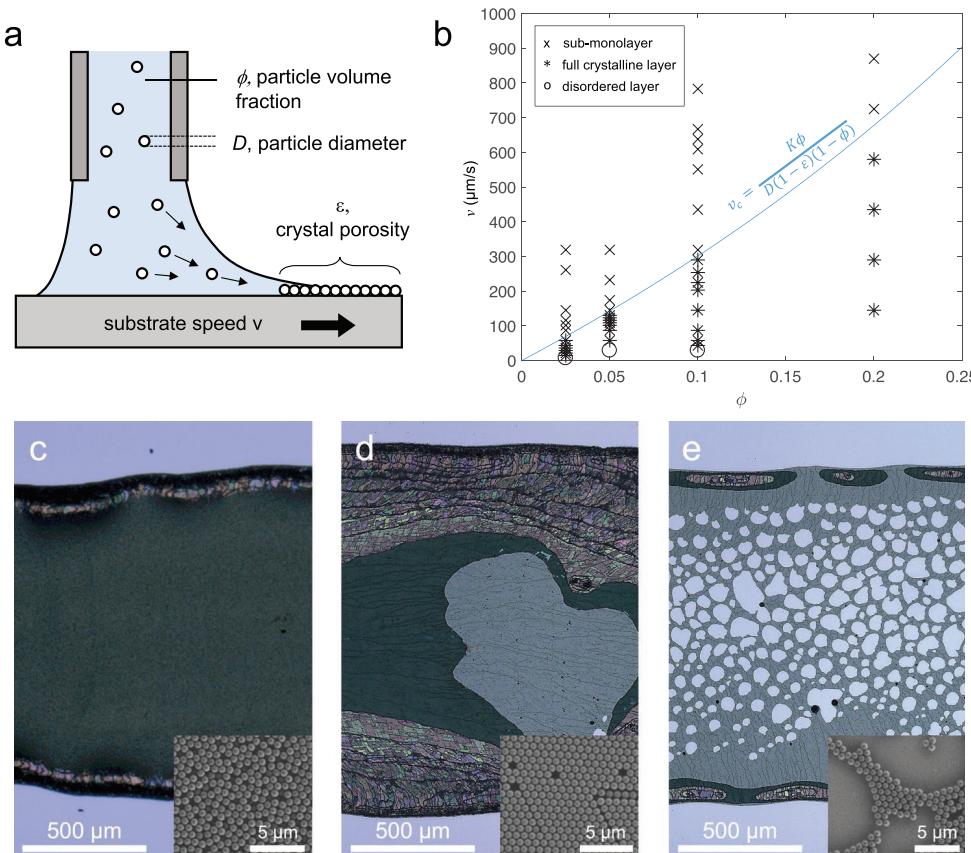


Figure 2. Optimization of direct-write process parameters to achieve well-packed crystalline deposits. a) Schematic of the direct-write assembly process, where ϕ is the volume fraction of particles in solution, D is the particle diameter, ε is the porosity of the colloidal crystal, and v is the substrate speed. b) An operational phase diagram where disordered, ordered, and sub-monolayer phases are plotted as a function of ϕ and v . The curve delineates the natural assembly speed as modeled by the Dimitrov-Nagayama equation with fitting parameter K . Optical microscope images and inset SEM of colloid trails with c) disordered, d) ordered, and e) sub-monolayer phases.

Figure 2a. Further, l is a characteristic evaporation length, j_e is the water evaporation flux, and β is an interaction parameter between 0 and 1, where $\beta = 1$ corresponds to complete entrainment of particles by water flux. A particle monolayer is denoted by $h = D$. By replacing the term $\beta l j_e$ with an experimentally fitted parameter K , as previously demonstrated by Prevo and Velev,^[25] we can create an operational phase diagram which maps the relationship between experimental variables and crystallinity of the deposited particles. From a series of experiments at different write speeds v and feedstock particle concentrations ϕ , we identified disordered, ordered, and sub-monolayer phases, as plotted in Figure 2b. The curve delineates the rate of crystal growth for a monolayer according to Equation (1), with $\varepsilon = 0.605$ (corresponding to hexagonal close packing) and $K = 8 \times 10^4 \text{ m}^2 \text{ s}^{-1}$. Below this line, ordered phases of at least single-particle thickness are obtained, such as shown in Figure 2d. Above the line, the write speed v exceeds the rate of crystal growth v_c , resulting in a sub-monolayer deposit, such as shown Figure 2e. Additionally, at very low speeds, the particles are deposited as disordered aggregates, such as shown in Figure 2c.

This information serves as a practical guide for high throughput direct-write self-assembly. As a case in point, the typical as-received concentration of commercial colloidal particles

is $\phi = 0.025$, which requires a write speed of $\approx 50 \mu\text{m s}^{-1}$ for the crystalline phase. However, by simply increasing the concentration of particles to $\phi = 0.2$ via centrifugation and decanting, the concentrated particle suspension can then be used to boost write speed by an order of magnitude to $\approx 600 \mu\text{m s}^{-1}$.

By motorized stage motion, a colloidal crystal can be directly patterned using a digital template (e.g., starting with a vector graphic, Figure S1, Supporting Information), without the need for further process steps such as etching. The colloid suspension is dispensed at a constant rate while translating the stage according to the script, resulting in a patterned colloidal crystal in the shape of the vector graphic, as shown in Figure 3.

The general iridescence visible throughout the colloidal crystal indicates a high degree of crystallinity. Conversely, the small regions that lack iridescence indicate lack of particle order. Specifically, these regions occur where there was a turn or overlap in the toolpath, suggesting that the toolpath trajectory can have a strong influence on self-assembly. Moreover, the local curvature of the toolpath affects order, and the limiting cases are revealed in Figure 3b-i, b-iii, and b-iv. In the limit of a straight line (Figure 3b-iii) or wide arc (Figure 3b-i), crystallinity is maintained. In contrast, in the limit of a sharp 90° turn (Figure 3b-iv), a white patch appears on the inside of the turn which indicates a region of disorder. Thus, the appearance of

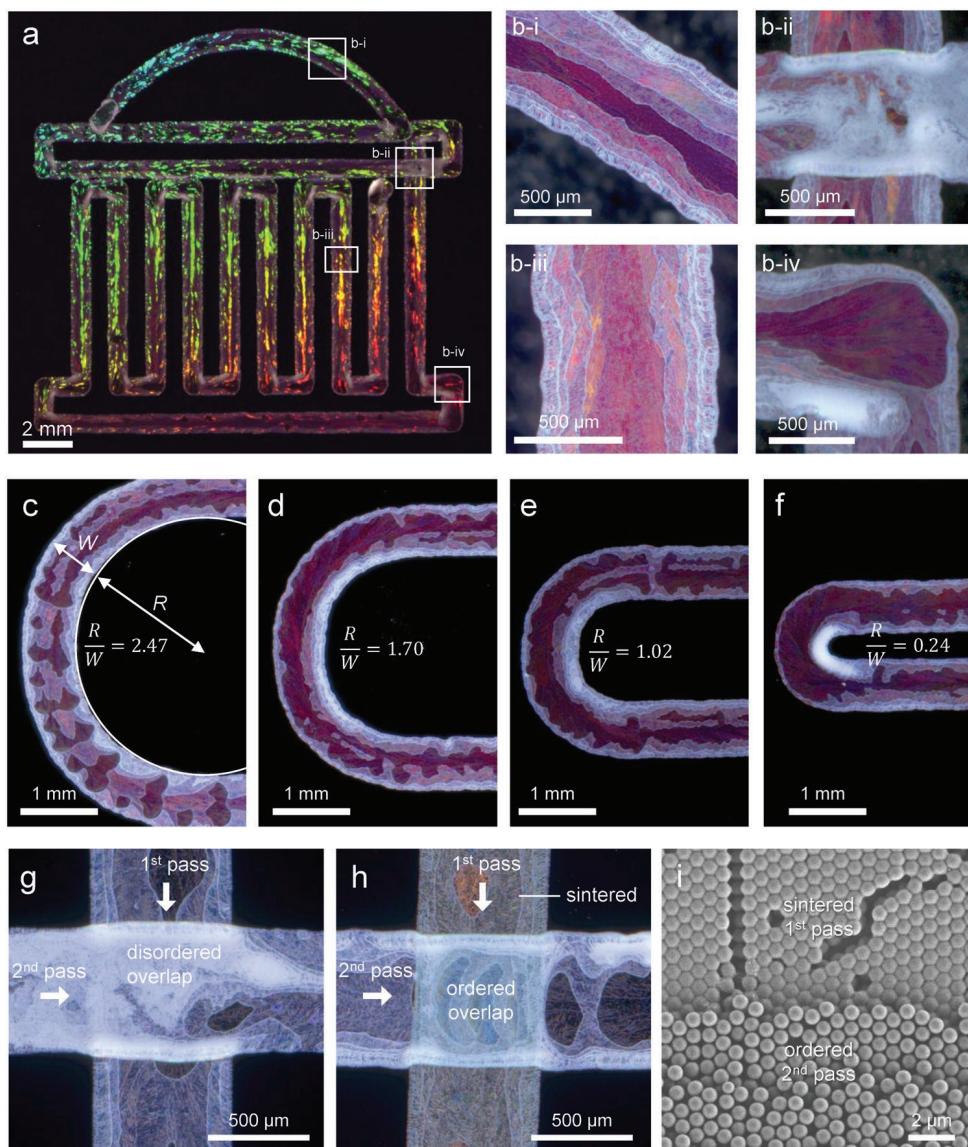


Figure 3. Effect of direct-write tool path on crystal order. a) Photograph of a colloidal crystal patterned by control of the direct-write trajectory. b) Optical microscope enlargements showing the morphology of a b-i) wide arc, b-ii) overlap, b-iii) straight line, and b-iv) sharp turn. The crystallinity of a colloidal trail is affected by curvature of the direct-write trajectory, as demonstrated by trails with turning radius (R) of c) 1.63 mm, d) 1.12 mm, e) 0.67 mm, and f) 0.16 mm, and constant width $W = 0.66$ mm. Generally, the inside of the curved trail is ordered when $R/W > 1$ but becomes disordered when $R/W < 1$. Optical images of perpendicular overlapping trails. g) Without sintering, overlapping colloidal trails result in disorder, as apparent from the whitish region on the trail from the second pass. h) After sintering of the trail from the first pass, the trail from the second pass is deposited atop with crystalline arrangement. i) SEM image of a sintered first pass and an ordered second pass.

iridescence provides visual feedback on the degree of order or disorder of the colloidal assembly.

Next, we performed a series of experiments with different tool path curvatures. We denote the inner radius of curvature as R and the width of the colloidal trail as W (Figure 3c). Micrographs shown in Figure 3c-f depict colloidal trails with progressively smaller R , yet constant W (governed by the needle diameter). In general, as R decreases relative to W , the deposit of particles on the inside of the turn becomes thicker and eventually becomes disordered when $R < W$. This observation is in general agreement with the phase diagram (Figure 2b), which shows that slow write speeds lead to disordered deposits.

The deposition rate of particles relative to the local tangential velocity is inversely proportional to the local curvature of the path. In the experimental conditions for Figure 3f, the volume fraction of particles is $\varphi = 0.05$ and the tangential velocity at the middle of the tool path is $v_1 = 146 \mu\text{m s}^{-1}$. The radius of curvature at the middle of the toolpath is $R_1 = 500 \mu\text{m}$ and the inside radius of curvature of the toolpath is $R_2 = 140 \mu\text{m}$. Therefore, the tangential velocity at the inside of the toolpath is $v_2 = (R_2/R_1)v_1 = 40 \mu\text{m s}^{-1}$. These conditions ($\varphi = 0.05$, $v_2 = 40 \mu\text{m s}^{-1}$) corresponds to the onset of disorder in Figure 2b.

The direct-write colloidal crystals exhibit structural colors that depend on the local crystalline order, lighting, and viewing

conditions. The primary mechanisms by which structural colors are commonly created are broadly categorized into thin film interference, multilayer interference, grating diffraction, and other interference phenomena; each is enabled by nano- to microscale periodicity on the order of the wavelength of visible light.^[26]

To characterize the light scattering and iridescence of a printed colloidal crystal, we illuminated the sample with collimated light such that the reflected light was projected onto the inside of a ping-pong ball, as illustrated in Figure 4c. This technique allows colors from all viewing angles to be visualized in a single image.^[27] A sample with small grains (prepared at $v = 610 \mu\text{m s}^{-1}$ with $\varphi = 0.10$) is shown in Figure 4a, and the corresponding color projection is displayed in Figure 4d. The separation of color leads us to hypothesize that the colloidal crystal acts as a reflective diffraction grating, because shorter wavelengths are diffracted at smaller angles with respect to the normal, as one would expect from the grating equation

$$m\lambda = d(\sin\theta_i + \sin\theta_r) \quad (2)$$

Where m is the diffraction order, d is the grating spacing, θ_i and θ_r are respectively the angles of incident and diffracted rays relative to the normal. In our experimental conditions, $m = 1$ since we observe only one diffraction order, $\theta_i = 0^\circ$ since the incident ray is normal to the sample, and $d = \sqrt{3}/2D$ since the particles are arranged in a hexagonal lattice with center-to-center distance of D .

The colors on the hemispherical screen in Figure 4d can be linearly mapped with respect to polar angle θ and azimuthal angle ϕ , yielding Figure 4e. From Figure 4e, the radiant intensity can be averaged over all values of ϕ and plotted as a function of θ for each of the camera's three color channels, as shown in Figure 4f. The peaks can be used, in conjunction with Equation (2), to estimate particle size by using $\lambda = 490, 550$, and 650 nm as the peak wavelengths for the blue, green, and red channels, respectively.^[28] This yielded an estimated particle diameter of 751 nm , which matches the known colloid diameter of $746 \pm 22 \text{ nm}$.

If there are many small colloidal crystal grains with different orientations present (such as for the sample shown in Figure 4a), each diffracting light toward a different azimuthal angle (ϕ), the scattered radiant intensity is almost constant along all azimuthal angles. However, if there are only a few grains present, distinct peaks are visible in the color projections. When the same experiment is performed with a large-grain sample (Figure 4b, prepared at $v = 30 \mu\text{m s}^{-1}$ with $\varphi = 0.025$), distinct diffraction peaks are observed, as shown in Figure 4g,h. The sixfold symmetry of the diffraction pattern projected onto the sphere indicates that the particles assume a hexagonal arrangement.

Moreover, by analyzing the relative intensities of the peaks, it is possible to deduce information about the size proportions of the grains present in the illuminated region. To perform this analysis, we extracted the radiant intensity as a function of the azimuthal angle ϕ at a polar angle $\theta = 52^\circ$ (see area marked in Figure 4h) and plotted the data as Figure 4i. Due to the sixfold symmetry of the diffraction pattern, the data is collapsed onto $\phi = 0$ to $\phi = 60^\circ$. The highest and second-highest peaks should

correspond to the largest and second-largest grains, which we designate as grains A and B, respectively. The radiant intensity level marked by the black solid line should then correspond to the much smaller grains of various orientations, which we designate as C. By comparing the relative peak intensities, we calculate that the area fraction of the various grain structures are $f_A = 0.41 \pm 0.14$, $f_B = 0.11 \pm 0.06$, and $f_C = 0.48 \pm 0.17$ (see the Supporting Information for description of calculation). This result may be compared to the direct measurement of relative grain sizes via image analysis. An optical micrograph of the illuminated region is shown in Figure 4j, with the A, B, and C structures identified and labelled. By image segmentation, we measured $f_A = 0.32$, $f_B = 0.09$, and $f_C = 0.59$. Given the large uncertainty in the peak signal for A, the estimates from the diffraction peak intensities are in reasonable agreement with the measurements from the micrograph. Finally, using SEM (Figure 4k), we measured that grains A and B are misoriented by 19.5° . This is in close agreement with the radiant intensity plot (Figure 4i), which shows the A and B peaks 20° apart.

Sequential deposition of particles in multiple write passes, such as in overlapping or intersecting patterns, could facilitate the use of colloidal assembly for 3D printing. However, we initially found that an overlap in the direct-write toolpath results in disorder, as shown in Figure 3b-ii. We hypothesize that this is due to the array of particles from the first pass being broken up by the liquid meniscus during the second pass. Therefore, if the particles from the first pass are effectively immobilized, then it may be possible to preserve crystallinity for multiple passes to build up 3D prints.

One means of immobilizing the particle array is to sinter the particles. To sinter the particles, a colloidal crystal sample was heated to 110°C for 15 min, followed by 1 min of oxygen plasma treatment. The oxygen plasma improves the wettability of the surface, which becomes hydrophobic after the heating step. The sintering causes a slight color change in the colloidal crystal due to necks forming between the particles, which reduces the interparticle spacing. A second pass of direct-writing was then performed atop the first pass, as shown in Figure 3h. Separately, a second pass of direct-writing was also performed on a control sample which was not sintered, as shown in Figure 3g. The preservation of structural color on the sintered sample, compared to the whitish regions on the control sample, shows that sintering was effective in immobilizing the particle array from the first pass, allowing the particles on the second pass to self-assemble on the sintered array with crystalline registry. SEM confirms particle order on the second pass for the sintered sample (Figure 3i), and particle disorder on the second pass for the control sample (Figure S2, Supporting Information). Potentially, layer-by-layer sintering (e.g., by in situ infrared heating) of the particles could be employed for building up multilayer structures with crystalline registry of the particles, which would be a means of 3D printing colloidal crystals.

Additionally, we explore how the direct-write technique could be employed to assemble diverse colloidal assemblies with the potential for more functionality. As a simple example, in Figure 5, we demonstrate direct-writing of colloidal crystals comprising of different particle sizes (500 nm, 746 nm, and 1 μm) and different particle compositions (PS, PMMA, and

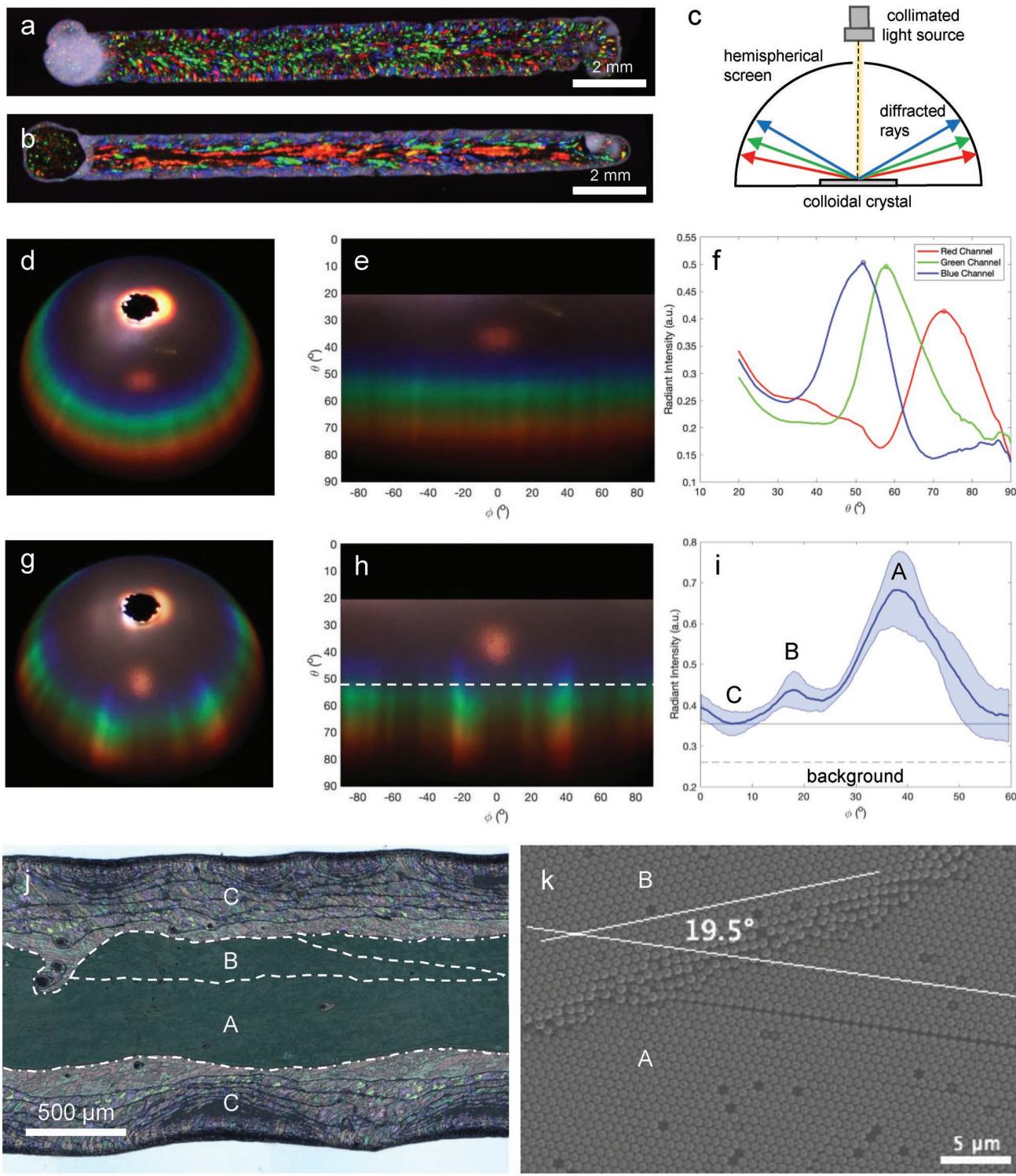


Figure 4. Optical properties of direct-write colloidal crystals. Photographs of a) small-grain and b) large-grain colloidal crystal imaged under ring lighting around the objective lens. c) Schematic depicting the characterization of optical properties by illuminating the colloidal crystal with collimated light at an angle normal to the crystal and observing the projection of diffracted colors on a hemispherical screen. Photograph of colors projected from the d) small-grain and g) large-grain colloidal crystal. Colors from the e) small-grain and h) large-grain samples linearly mapped onto azimuthal angle ϕ and polar angle θ . f) Plot of radiant intensity versus θ for each of the RGB channels, obtained by averaging over all values of ϕ . i) Plot of radiant intensity versus azimuthal angle ϕ derived from the blue channel of (h), ranging $\phi = 0^\circ$ – 60° averaged over the sixfold symmetry regions, at $\theta = 52^\circ$. The solid blue line is the radiant intensity and the shaded region represents standard deviation. The highest peak is from the largest grain, A; the second highest peak is from the second-largest grain, B; and the lowest radiant intensity, denoted by the solid black line, is an estimate of the amount of light from various other small grains, C. The dashed line represents the background illumination of the ping pong ball, measured in a noncolored region. j) Optical image of the illuminated region, with A, B, and C grain structures identified. k) SEM image analysis confirms that the largest grain A and the second-largest grain B are relatively orientated at 19.5° .

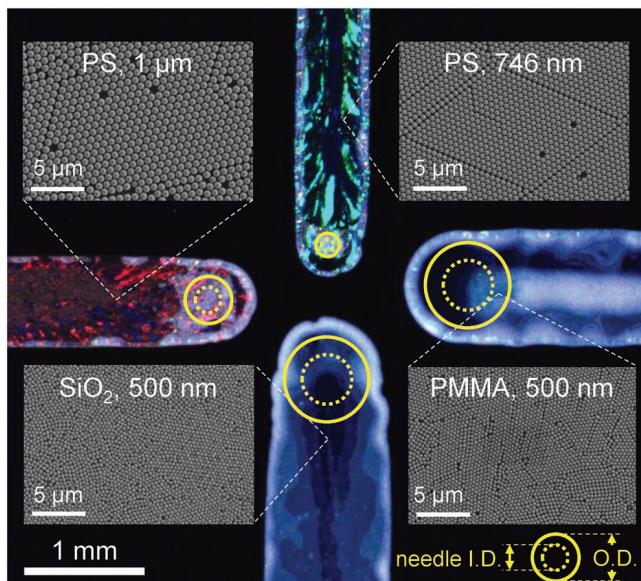


Figure 5. Direct-write fabrication of multiple colloidal materials on the same substrate. Clockwise from top: 746 nm polystyrene (PS) particles with a needle of OD, ID = 0.2, 0.1 mm; 500 nm polymethylmethacrylate (PMMA) particles with a needle of OD, ID = 0.7, 0.4 mm; 500 nm silica particles with a needle of OD, ID = 0.7, 0.4 mm; 746 nm polystyrene particles with a needle of OD, ID = 0.4, 0.2 mm. The needle diameters are overlaid on the respective colloidal crystal.

silica) on the same silicon wafer. Figure 5 also demonstrates the limits to the width of the crystal that can be controlled by the diameter of the needle. Although smaller needles may be used for direct-write assembly, the width of the crystal is not strictly proportional to the diameter of the needle, as shown from the progression of needle sizes from 22 gauge (OD, ID = 0.7, 0.4 mm) to 27 gauge (OD, ID = 0.4, 0.2 mm) to 33 gauge (OD, ID = 0.2, 0.1 mm). With the smallest needle size, 33 gauge, the crystal width was similar to that of the 27 gauge due to spontaneous spreading of the liquid meniscus that is difficult to control even at very low dispense rates (1.57 nL s^{-1}), as shown in Figure S3 (Supporting Information). Yet, spreading of the liquid meniscus at a finite contact angle is necessary for successful deposition of particles.^[29,30] Future work on direct-writing of colloids could include exploring the technique's ultimate resolution limits by tuning the hydrophilicity of the surface via plasma treatment or pre-depositing molecular self-assembled monolayers onto the substrate to control spreading of the meniscus.

In conclusion, we demonstrated freeform fabrication of colloidal crystals by in-plane direct-write self-assembly, and experimentally derived an operational phase diagram, which maps write speeds and particle concentrations that lead to crystalline features. Furthermore, we investigated the effect of tool-path trajectory on the crystallinity of the colloidal assemblies, and showed that sintering can be used to stack overlapping passes. We also established grating diffraction as the mechanism for the structural color effects in these colloidal crystals, and showed that simple characterization of the optical properties of the crystals yields reliable information about microstructure, such as particle size, grain size, and orientation. In future work, in-plane direct-write assembly could be extended

to a practical technique for 3D printing of colloidal crystals if a means for rapidly sintering each layer could be developed. Finally, we note that, while macroscopic printed features can be well-controlled by the direct-write toolpath, at the microstructural level, every trace or image that is printed with direct-write is unique, which suggests applications of direct-write in generating patterns for use in optical encoding and security devices.

Experimental Section

Direct-Write Self-Assembly: An aqueous suspension of polystyrene particles (750 nm diameter, Polysciences Inc.) was loaded into a 100 μL syringe (Hamilton 1710 RN) affixed with a blunt tip needle (Hamilton point style 3, 27ga) and placed into a custom-made holder. The plunger of the syringe was depressed using a linear actuator (M-229.26S, Physik Instrumente) commanded from a computer. The stage was heated to $30 \pm 0.1^\circ\text{C}$ by a thermoelectric chip (Custom Thermoelectric) and the stage temperature was measured by an embedded K-type thermocouple (Omega) fed to a temperature controller (PTC 10, Stanford Research Systems). The stage was actuated by linear motors (Zaber LRM025A E03T3MC03) controlled by a two-axis stepper motor controller (Zaber XMCB2 KX14B) via the Zaber Console software. To perform direct-write in complex trajectories, the shapes were drawn using Carbide Create software, and the G-code was converted into native motor commands using the G-code translator in the Zaber Console software.

Microstructural Characterization: Optical images were taken using a Zeiss Smartzoom optical microscope. Images were taken in coaxial lighting mode (Figures 1c, 2c–e, 4j) to clearly distinguish monolayers, bilayers, and multilayers. Images were taken in ring lighting mode (Figures 3a,b, 4a,b, 5) to clearly distinguish iridescent and noniridescent regions. SEM was performed with a Zeiss Merlin High Resolution SEM in high efficiency secondary electron imaging mode, at an accelerating voltage of 1 kV and probe current of 100 pA. Image analysis was performed using ImageJ.

Characterization of Optical Properties: The colloidal crystal sample was illuminated by a light source (Ocean Optics HL-2000) directed by an optical fiber (Thorlabs M25L01, $\phi 200 \mu\text{m}$, 0.22 NA) to a collimating lens (Thorlabs F230SMA-A, alignment wavelength = 543 nm, $f = 4.34 \text{ mm}$, NA = 0.57). The collimated light was directed to shine through a hole drilled through a translucent hemispherical screen (half a ping pong ball) and onto the sample placed in the middle of the enclosing hemisphere. The light projected onto the screen was recorded with a DSLR camera (Canon EOS Rebel T3i) which was fixed in position using an articulated arm.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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