Supplementary Materials for

Direct writing of customized structural-color graphics with colloidal photonic inks

Jong Bin Kim, Changju Chae, Sang Hoon Han, Su Yeon Lee, Shin-Hyun Kim*

*Corresponding author. Email: kim.sh@kaist.ac.kr

Published 24 November 2021, Sci. Adv. 7, eabj8780 (2021)
DOI: 10.1126/sciadv.abj8780

The PDF file includes:

- Supplementary Text
- Figs. S1 to S35
- Legends for movies S1 to S10

Other Supplementary Material for this manuscript includes the following:

- Movies S1 to S10
**Supplementary Text**

S1. Threshold volume fraction for colloidal crystallization

Silica particles dispersed in acrylate-based resin have a solvation layer on the surface through hydrogen bonds between the silanol group on the surface and the acrylate group of the resin. The solvation layer renders the dispersion stable by exerting interparticle repulsion (36). When the volume fraction of particles is high enough to overlap the solvation layers between adjacent particles at average separation, the particles spontaneously crystallize to minimize the repulsive energy. To investigate the threshold volume fraction for the spontaneous crystallization, we measure the storage and loss moduli, \( G' \) and \( G'' \) for various volume fractions of \( \phi = 0.10 \) and higher in the resins of EA and UA (fig. S1); carbon black nanoparticles with an average diameter of 24 nm are additionally dispersed in the resin at the concentration of 0.05% w/w in a silica-free resin basis for all inks. The oscillatory test is carried out through frequency sweep in a range of 0.1 – 100 rad s\(^{-1}\) while fixing a strain amplitude at 5%.

For EA inks, the loss modulus is higher than the storage modulus (\( G'' > G' \)) in the frequency lower than 50 rad s\(^{-1}\) for the volume fraction of \( \phi = 0.10 \) (fig. S1A). That is, the dispersion behaves more like a viscous liquid in most timescale (35, 36). For the volume fraction of \( \phi = 0.20 \) or higher, the storage modulus is larger than the loss modulus (\( G' > G'' \)) in the entire range of frequency. As particles have strong interparticle repulsion in the short-range, there is no chance for them to make aggregation with large voids at the volume fraction of \( \phi = 0.20 \). Therefore, the crossover of \( G' \) and \( G'' \) between \( \phi = 0.10 \) and 0.20 is attributed to the crystallization of particles. Each particle in a nonclose-packed crystalline lattice is force-balanced by repulsive interparticle potentials from its neighbors, which makes the lattice behave more like a solid than a liquid. It seems that average interparticle separation is too large to overlap the solvation layers at \( \phi = 0.10 \) while the solvation layers begin to be universally overlapped in the entire dispersions at \( \phi = 0.20 \). The films produced by infiltration of the dispersion into a gap between two glass slides and photocuring show structural colors and reflectance peak for the dispersions with \( \phi = 0.20 \) or higher while that for \( \phi = 0.10 \) doesn’t.

For UA inks, a similar trend is observed (fig. S1B). At \( \phi = 0.10 \), the loss modulus is higher than the storage modulus (\( G'' > G' \)) in the frequency lower than 50 rad s\(^{-1}\) for the volume fraction of \( \phi = 0.10 \) (fig. S1A). That is, the dispersion behaves more like a viscous liquid in most timescale (35, 36). For the volume fraction of \( \phi = 0.20 \) or higher, the storage modulus is larger than the loss modulus (\( G' > G'' \)) in the entire range of frequency. As particles have strong interparticle repulsion in the short-range, there is no chance for them to make aggregation with large voids at the volume fraction of \( \phi = 0.20 \). Therefore, the crossover of \( G' \) and \( G'' \) between \( \phi = 0.10 \) and 0.20 is attributed to the crystallization of particles. Each particle in a nonclose-packed crystalline lattice is force-balanced by repulsive interparticle potentials from its neighbors, which makes the lattice behave more like a solid than a liquid. It seems that average interparticle separation is too large to overlap the solvation layers at \( \phi = 0.10 \) while the solvation layers begin to be universally overlapped in the entire dispersions at \( \phi = 0.20 \). The films produced from UA dispersion at \( \phi = 0.20 \) show structural colors and reflectance peaks of crystalline arrays when the dispersion is incubated for several days before the photocuring. That is, the threshold volume fractions, \( \phi_{th} \) for crystallization of silica particles in both EA and UA resins are between 0.10 and 0.20.

S2. Transition from viscoelastic liquid to brittle solid

As the volume fraction of particles increases, so do the dynamic moduli and viscosity. There is a transition from a viscoelastic liquid to a brittle solid at which the dispersions completely lose fluidity. The volume fraction at the transition, \( \phi_{tr} \), depends on dispersion medium and particle size (29). For EA inks, the transition is observed at \( \phi_{tr} \sim 0.54, 0.53, \) and 0.52 for silica particles with diameters of \( d = 226 \) nm, \( 190 \) nm, and \( 175 \) nm, respectively (fig. S2). The transition volume
fractions are slightly increased to $\phi_t \sim 0.58$, 0.57, and 0.56 for PEA inks and slightly decreased to $\phi_t \sim 0.45$, 0.43, and 0.40 for UA inks, respectively.

The volume fractions at the liquid-to-solid transition for all three resins are far below the maximum volume fraction of closely-packed spheres in face-centered cubic (fcc) or hexagonal close-packed (hcp) lattice, 0.7404 and smaller than the random close packing (rcp), approximately 0.64. That is, the transition occurs in the absence of physical contact among silica particles. It seems that all resin molecules are strongly bound on the surface of silica particles at the transition so that no lubrication layers exist among the particles. That is, the solvation layer is composed of two regions: 1) mobile outer region of loosely-bound molecules and 2) immobile inner region of strongly-bound molecules. Above the threshold volume fraction of crystallization, the outer solvation layers of loosely-bound molecules are overlapped, which causes the silica particles to form nonclose-packed arrays. At the transition volume fraction, no mobile outer layer is available, leading to a transition from liquid to solid (fig. S3).

The thicknesses of the solvation layer and immobile inner region, $l_s$ and $l_{in}$ can be approximately estimated from the threshold and transition volume fractions, respectively. Assuming that the silica particles form a nonclose-packed fcc lattice at the threshold volume fraction, we obtain

$$\phi_{th} = \frac{4 \times \pi d^3}{a^3}, \quad \text{(Equation S1)}$$

where $a$ is a lattice constant. As the center-to-center distance between two nearest neighbors, $d_{cc}$, is $a/\sqrt{2}$,

$$l_s = \frac{1}{2} (d_{cc} - d) = \frac{1}{2} \left( \frac{\pi}{3 \sqrt{2} \phi_{th}} \right)^{1/3} - 1 d = \frac{1}{2} \left( \frac{0.7404}{\phi_{th}} \right)^{1/3} - 1 d. \quad \text{(Equation S2)}$$

From $\phi_{th} \sim 0.15$ and $d = 190$ nm, we roughly estimate the thickness of the solvation layer as $l_s \sim 59.1$ nm for both EA and UA inks.

At the transition volume fraction, particles form amorphous arrays rather than crystalline structures. Therefore, the maximum fraction of particles for close packing is approximately 0.64 when the arrangement is maintained. The thickness of the immobile inner region, $l_{in}$, is roughly estimated from the transition volume fraction, $\phi_t$:

$$l_{in} \sim \frac{1}{2} \left( \frac{0.64}{\phi_t} \right)^{1/3} - 1 d. \quad \text{(Equation S3)}$$

For EA inks, $\phi_t \sim 0.54$, 0.53, and 0.52 for silica particles with diameters of 226 nm, 190 nm, and 175 nm, from which $l_{in,EA} \sim 6.3$ nm. In the same manner, $l_{in,PEA} \sim 3.8$ nm and $l_{in,UA} \sim 13.3$ nm for PEA and UA inks, respectively. Therefore, the transition volume fraction is approximated for any diameter of particles:

$$\phi_{tr} \sim 0.64 \left( 1 + \frac{2l_{in}}{d} \right)^{-3}. \quad \text{(Equation S4)}$$

A higher transition volume fraction is expected for larger particles from Equation S4 as experimentally confirmed. This is attributed to the lower surface area so that the inner region of the solvation layer holds a smaller volume of resin molecules.
S3. Optimum volume fraction

The volume fraction of silica particles should be carefully selected to produce particle arrays with the controlled arrangement. At the same time, the inks should satisfy rheological conditions for direct writing. For EA, the crystalline structure can be obtained as long as the volume fraction exceeds the threshold for crystallization. However, the volume fraction slightly larger than \( \phi_{th} \) renders the dispersions highly fluidic. Low viscosity causes the overdose even at the minimum controllable pneumatic pressure of 3 kPa because the volumetric flow rate is inversely proportional to the viscosity. In addition, the dispersions leak out even after pressure is off as the characteristic timescale for stopping a Poiseuille flow is also inversely proportional to the viscosity. Furthermore, lines are broadened by fast spreading. For example, the lines are wide in the middle and dog-bone-shaped at the ends when the volume fraction of 0.33 in EA is used (fig. S4A). Also, the intersection between two crossed lines gets broader due to fast spreading. By contrast, volume fraction slightly smaller than \( \phi_{tr} \) provides high printability. For example, the lines are straight and the intersection of lines shows no wide-spreading when the volume fraction is set to be smaller than \( \phi_{tr} \) as much as 0.005 (fig. S4C); \( \phi_{tr} \sim 0.54 \). However, the colloidal particles form amorphous arrays, developing matte structural colors. When the volume fraction is lowered as much as 0.02 from \( \phi_{tr} \), both high printability and crystalline structures are secured (fig. S4B). For PEA inks, the volume fractions of \( \phi_{tr} - 0.02 \) provide high printability and crystalline structures in the same manner as EA inks. For UA inks, the crystalline arrays are obtained only for the volume fraction close to \( \phi_{th} \) if the inks are incubated for a sufficiently long time. Due to the ultra-high viscosity of UA resin, the particles form amorphous arrays in a wide range of volume fractions between \( \phi_{th} \) and \( \phi_{tr} \). The high printability is secured for the volume fractions of \( \phi_{tr} - 0.02 \). Therefore, the volume fractions are optimized as \( \phi_{opt} = \phi_{tr} - 0.02 \) for all three resins of EA, PEA, and UA. That is, \( \phi_{opt,EA} = 0.64 \left( 1 + \frac{12.6 \text{nm}}{d} \right)^{-3} - 0.02 \), \( \phi_{opt,PEA} = 0.64 \left( 1 + \frac{7.6 \text{nm}}{d} \right)^{-3} - 0.02 \), and \( \phi_{opt,UA} = 0.64 \left( 1 + \frac{26.6 \text{nm}}{d} \right)^{-3} - 0.02 \) for EA, PEA, and UA, respectively. However, the volume fractions in the range between \( \phi_{tr} - 0.05 < \phi < \phi_{tr} - 0.01 \) are generally acceptable for printing.

In summary, EA and UA show a similar trend for the arrangement of silica particles (fig. S5). In low volume fractions, particles are randomly dispersed without any order. As the volume fraction exceeds the threshold for crystallization, \( \phi_{th} \), the particles crystallize to have a long-range order. As the volume fraction further increases, particles form an amorphous array with a short-range order only. Finally, the dispersions turn to solid with no fluidity at the volume fraction for a liquid-to-solid transition, \( \phi_{tr} \). However, the range of volume fraction for the crystallization is very different due to the large contrast of viscosities of particle-free resins. For EA (or PEA) with moderate viscosity, silica particles crystallize for a wide range of volume fractions of \( \phi_{th} \leq \phi \leq \phi_{tr} - 0.01 \). When \( \phi \sim \phi_{tr} \), the silica particles form an amorphous array as the energy barrier for rearrangement is too high at the liquid-to-solid transition. By contrast, silica particles crystallize only for \( \phi \sim \phi_{th} \) and form amorphous arrays in the most range of volume fractions of \( \phi > \phi_{th} \) in UA with a high viscosity. That is, the energy barrier for the rearrangement is too high even for the volume fraction slightly larger than \( \phi_{th} \) due to the high intrinsic viscosity of UA.
S4. Angle dependence of structural colors for direct-written lines
The lines are direct-written to have either crystalline or amorphous colloidal arrays by using EA or UA inks, respectively (fig. S6). To compare angle dependence of structural colors for the crystalline and amorphous arrays, the lines are observed at specular reflection conditions (fig. S6A). Both lines show a blue shift of the colors with the increasing angle (fig. S6, B and C). However, the magnitude of the blue shift is larger for the crystalline arrays than the amorphous array. For the comparable reddish color for normal reflection, the crystalline array shows a greenish color at the angle of 30°, whereas the amorphous array shows a reddish one at the same angle. At the angle of 80°, the crystalline arrays show a bluish color, whereas the amorphous array shows a greenish color. CIE diagram also supports the different magnitude of the blue shift (fig. S6D and E). Although the amorphous arrays show orientation-independent structural colors, they are not completely non-iridescent. The amorphous arrays show a blue shift of structural color with the increasing angle at the specular reflection although the magnitude is smaller than the crystalline counterpart.

S5. Shear-thinning and thixotropic relation
The viscosity of dispersions significantly decreases along with the shear rate for both EA and UA inks, which improves the ease of printing (32-34). For an EA ink with $\phi_{opt} = 0.51$ and $d = 190$ nm, the viscosity gradually decreases from $1.6 \times 10^6$ mPa·s to $1.4 \times 10^3$ mPa·s as the shear rate increases from $10^3$ s$^{-1}$ to 40 s$^{-1}$ (fig. S7A); the viscosity of pure EA resin is 50 mPa·s which is shear-independent. In a typical printing condition, the shear rate in the nozzle is approximately 10 s$^{-1}$ so that the viscosity is approximately $2.3 \times 10^3$ mPa·s during the printing. Immediately after the deposition on the target surface, the shear is discontinuously removed. However, the dispersions are not able to recover the shear-free viscosity immediately because it takes time for the particle rearrangement (35). To estimate the timescale for the recovery, we use the thixotropic test. The shear rate is increased from 0.01 s$^{-1}$ to higher shear rates of 0.1 s$^{-1}$, 1 s$^{-1}$, 10 s$^{-1}$, and 25 s$^{-1}$, respectively, which are then suddenly decreased to the original rate of 0.01 s$^{-1}$. For the abrupt increases of shear rate, the viscosity drops without a delay (fig. S7B). By contrast, it takes around 30 s for the dispersions to recover the original viscosity for the abrupt change to the original shear rate. Therefore, it is expected that the EA inks rapidly spread on target surfaces immediately after the deposition and the spreading gradually slows down in 30 s.

We measure the viscosity for an UA ink with $\phi_{opt} = 0.41$ and $d = 190$ nm. The UA inks show shear-thinning behavior for the shear rates up to 0.26 s$^{-1}$ (fig. S8A). For higher shear rates, the viscosity slightly increases and reaches a plateau in the range of shear rate, 1 s$^{-1}$ – 10 s$^{-1}$. It is noteworthy that the viscosity of pure UA resin is 7,000 mPa·s, which is two orders of magnitude higher than that of pure EA resin. In a typical printing condition, the viscosity is approximately 80,000 mPa·s so that the UA inks require higher pneumatic pressure for the printing than the EA inks. In the thixotropic test, the viscosity is rapidly increased in 150 s after the sudden decrease of the shear rate (fig. S8B). However, the viscosity is not fully recovered and remains at 85% of the original viscosity in 300 s. That is, UA inks require a much longer time to completely recover the original arrangement, possibly due to the high viscosity of UA resin. Therefore, the spreading of UA inks lasts longer than EA inks.
S6. Shear-dependent evolution of colloidal arrangement
When dispersions are sheared, the particle arrangement is changed, which influences dynamic moduli. From the changes of the moduli, the structural transformation can be roughly estimated (35). For EA ink with $\phi_{\text{opt}} = \phi_u - 0.02 = 0.51$ and $d = 190$ nm, storage and loss moduli, $G'$ and $G''$, are measured from an oscillatory test with a strain sweep at a fixed frequency of 1 Hz (fig. S9A). There is a linear viscoelastic region in the shear-stress range of 0.04 – 3 Pa at which $G'$ and $G''$ remain almost unchanged (36). The constant moduli imply that the colloidal arrangement is rarely changed by the shear. It is expected that the dispersion is composed of small crystallites with various orientations in the linear region. Following the linear region, there is an overshoot of loss modulus around the shear stress of 9 Pa (37). We attribute this to the build-up of crystalline structure (fig. S9, C and D). As the shear causes the small crystallites to align along the flow direction, the crystallites are prone to be fused with their neighbors. The reduction of grain boundary by fusion leads to the increase of loss modulus by strongly localizing the shear flow at the boundary (fig. S9D). Afterward, there is a reduction of both storage and loss moduli along with strain, implying that the crystalline domains break down (fig. S9E) (35). It seems that the particles get closer within the same domain as the volume of particle-depleted boundary increases by the breakage. With a typical printing condition, the dispersions experience a shear rate of 10 s$^{-1}$ and shear stress of 23 Pa in the nozzle. When the printed lines are instantly captured by photopolymerization, a string-like arrangement of silica particles is observed (fig. S9B) (38, 39).

To further prove the evolution of colloidal arrangement with direct observation, the inks are sandwiched by a pair of parallel slide glasses with a separation of 120 μm and sheared by moving one of the slide glasses. The shear rate is manually set to be around 0.01, 1, and 100 s$^{-1}$, respectively. The inks are immediately photopolymerized by UV irradiation and the cross-sections of the resulting films are observed with SEM. At the shear rate of 0.01 s$^{-1}$, small crystalline domains with random orientation are observed (fig. S9C). The crystalline domains grow at the rate of 1 s$^{-1}$ (fig. S9D) and merge to have a single orientation parallel to the shear direction at the rate of 100 s$^{-1}$ (fig. S9E). Although the fragmentation into monolayers is difficult to confirm with the direct observation, the build-up and alignment of orientation along the shear are clearly observed.

We also measure the dynamic moduli for the UA inks with $\phi_{\text{opt}} = \phi_u - 0.02 = 0.41$ and $d = 190$ nm (fig. S10). There are almost no changes of $G'$ and $G''$ in a wide range of shear stress, 0.02 – 13.2 Pa. That is, the dispersions maintain the amorphous array without structural transformation in the linear viscoelastic region. The value of $G'$ decreases for the increase of shear stress from 13.2 to 52.7 Pa. The reduction of $G'$ is possibly caused by a breakage of the amorphous array by shear force. But, there is no reduction of $G''$ and both $G'$ and $G''$ increases along with the shear stress. These peculiar rheological behaviors are attributed to the UA resin with a high molecular weight of 1400 g mol$^{-1}$ rather than the change of colloidal arrangement. Polymer molecules stretch under high shear force along the flow direction. As the UA molecules are confined in the narrow interstitial voids among silica particles at the volume fraction as high as $\phi_{\text{opt}} = 0.41$, they experience a very strong shear rate, which may cause the stretching, increasing $G'$ and $G''$.

S7. Flow conditions during and after deposition
The inks are discharged from a moving nozzle tip and deposited on a stationary target surface. This printing can be considered as a set of a stationary nozzle and a moving surface. In the gap between the nozzle and target surface, the inks experience position-dependent shear flow. We superpose a vertical Poiseuille flow in the nozzle and a horizontal Couette flow in the gap to
roughly estimate the velocity profile in the inks at the gap. The vertical Poiseuille flow in the nozzle with an inner radius, $R$, has a parabolic profile:

$$v_z = 2 \frac{Q}{\pi R^2} \left(1 - \left(\frac{x}{R}\right)^2\right),$$  \hspace{1cm} (Equation S5)

where $Q$ is the volumetric flow rate. The horizontal Couette flow in the gap distance of $h$ for a writing speed, $s$, has a linear profile:

$$v_x = s \frac{z}{h}.$$  \hspace{1cm} (Equation S6)

With a typical printing condition of $R = 100 \mu m$, $h = 100 \mu m$, $s = 3 \text{ mm/s}$, and $Q = 8.9 \times 10^7 \mu m^3/s$, the velocity distribution is obtained (fig. S11); $Q$ is experimentally measured from the volume of dispensed lines. The velocity vectors are almost vertical in the middle whereas those are tilted as much as 45° near the top-right corner.

The inks spread after being deposited on the target surface. As expected from the thixotropic tests, the spreading is rapidly slowed down for EA inks and prolongs for UA inks. To estimate the shear rate for the spreading, the dispensed lines are instantly captured by photopolymerization, from which surface profiles are measured at various positions. With the writing speed, the position from the nozzle can be converted to spreading time after the deposition. For EA inks, the profile change gradually slows down in 7 s and no significant spreading is observed afterward (fig. S12). For the initial 1.5 s, the shear rate is estimated as 1.03 s$^{-1}$ from the comparison of two profiles at 0 and 1.5 s; the shear rate is calculated by $Ah^{2}r^{-1}$, where $A$ is one-quarter of the areas formed by two profiles, $h$ is the height of the intersection, and $t$ is a time interval. The shear rate decreases to 0.51 s$^{-1}$ for the next 2.5 s which is obtained from two profiles at 1.5 s and 4.0 s. The shear rate further decreases to 0.39 s$^{-1}$ for the next 3 s.

For UA inks, the spreading is relatively slow and lasts for several hours (fig. S13). For the initial 3 s, the shear rate is estimated as 0.108 s$^{-1}$, which is 0.114 s$^{-1}$ for the next 4 s. For the following 3 h, the spreading continues and the average shear rate is $1.01 \times 10^{-4}$ s$^{-1}$.

S8. Colloidal arrangement in printed lines

To investigate the colloidal arrangement in the lines of EA inks after thermal annealing, SEM images are taken on various spots on the top surface and cross-section. Both top surface and cross-section near the top show square arrays of silica particles, corresponding to (200) planes of an fcc lattice (fig. S14, A to C). That is, the top region of the lines has an fcc lattice whose [200] direction is aligned to be vertical on the top surface. When the lines are sliced along the angle of 45°, the cutting plane shows an arrangement that corresponds to (220) plane (fig. S14D), further clarifying the orientation of an fcc lattice. This abnormal orientation in the top region of the lines is attributed to the oblique flow direction in the ink that forms the top surface of the line during the deposition (the top-right corner in fig. S11). Under a strong shear flow, the silica particles form a string-like arrangement along the flow direction in EA inks (fig. S9B). Therefore, the strings are aligned obliquely along the writing direction. As the string-like arrangement is formed along the [220] direction of an fcc lattice, the fcc is produced by aligning the [220] direction at the angle of 45° during thermal annealing, thereby resulting in (200) planes along the top surface and normal cross-section. It is noteworthy that the square arrays on the top surface are always aligned to have their diagonal parallel to the writing direction as a result.

In the middle of lines, the cross-sections show that the string-like arrangement, [220] direction, is vertically aligned (fig. S15). This peculiar alignment is also caused by the almost vertical flow direction in the middle of the ink during the deposition (the middle in fig. S11). In the bottom of lines, the cross-sections show that the string-like [220] direction aligns horizontally
along the bottom surface, indicating that [111] direction is vertically aligned (fig. S16). This normal alignment is attributed to the rearrangement of silica particles during the spreading of lines after the deposition on the target surface rather than the flow direction at the moment of deposition. As the spreading causes a shear flow only on the dispersion near the bottom side, the rearrangement is localized.

The relative portion of each orientation of an fcc lattice is investigated through SEM analysis (fig. S17). In the line with a width of 462 μm and a height of 42.3 μm, the top region with vertically-aligned [200] direction has a thickness of approximately 6 μm – 7 μm along the top surface. The bottom region with vertically aligned [111] direction is approximately 4-μm-thick on the center and 11-μm-thick on the off-center; the thickness increases along the lateral direction from the center to the edge due to stronger shear force during the spreading. The middle region with vertically aligned [220] direction is approximately 30-μm-thick in the center, which gets thinner along the lateral direction from the center to the edge.

The crystalline structures of the direct-written line are also examined with the reflection spectra. As reflectance peaks are developed by Bragg diffraction from crystal planes of non-close-packed fcc lattice, the spectra reveal the orientation of crystal planes and relative thicknesses. The peak position for (hkl) planes, \( \lambda_{hkl} \), is expressed by the Bragg equation:

\[
\lambda_{hkl} = 2n_{eff} d_{hkl} = 2 \sqrt{\frac{1}{h^2 + k^2 + l^2}} \left( \frac{2\pi}{3\phi} \right)^{\frac{1}{3}} D \left( n_p^2 \phi + n_m^2 (1 - \phi) \right)^{\frac{1}{2}},
\]

(Equation S7)

where \( n_{eff} \) is the effective refractive index, \( d_{hkl} \) is the interplanar distance of (hkl) planes, \( \phi \) is the volume fraction of colloids, \( D \) is silica particle diameter, and \( n_p \) and \( n_m \) are refractive indices of particle and matrix, respectively. The spectra are acquired from the topmost region and edge region of lines (fig. S18). On the topmost region, the main peak appears at 599 nm, which is roughly consistent with \( \lambda_{111} = 606 \) nm; \( \phi = 0.52, D = 226 \) nm, \( n_p = 1.45, \) and \( n_m = 1.471 \). There is a subpeak at 523 nm, which coincides with \( \lambda_{200} = 525 \) nm. As we inspected in the cross-section, (200) planes, (220) planes, and (111) planes are stacked from the top surface (Fig. 1J). Therefore, both (200) and (111) planes develop peaks, while (220) planes have a peak at \( \lambda_{220} = 373 \) nm which is out of the range of spectral measurement. Near the edge, (111) planes occupy almost 50-70% of the entire thickness, which results in a single peak at 599 nm without a subpeak.

The lines drawn using UA inks show consistent amorphous arrays in all the positions in the cross-section after thermal annealing (fig. S19). No long-range order is observed even near the top and bottom surfaces. The reflectance spectrum acquired from lines written with UA ink shows a relatively broad and low peak (fig. S20).

S9. Influence of printing parameters on the formation of lines

For printing, we use a tapered nozzle whose tip is straight. The tip has an inner diameter of 200 μm and an outer diameter of 400 μm. When the inks are discharged from the nozzle with a typical pneumatic pressure condition, they show no die swell yet eject straight in the absence of the target surface. With the target surfaces, the inks are deposited, forming a line along the trajectory of nozzle movement. To draw lines with a consistent width, the volume of inks in the gap between the nozzle and target surface remains unchanged while maintaining contact with the surface. If the nozzle moves too fast in comparison with the ejection rate, the inks repeatedly contact the surface and retract back to dangling drop, forming a wavy line or series of dots (fig. S21). Therefore, there is an optimum window for pneumatic pressure and writing speed at the given gap distance.
The volumetric flow rate increases along with pneumatic pressure for both EA and UA inks (fig. S22A); the flow rates are measured from the volume of dispensed lines by considering the writing speed. As the viscosity of EA inks is lower than UA inks, the volumetric flow rates are higher. The flow rate is further influenced by gap distance and writing speed (fig. S22B). The narrower gap exerts larger hydrodynamic resistance, which results in a lower flow rate. On the other hand, the flow rate increases along with the writing speed although the increase is less significant than the gap distance. As the writing removes the highly viscous inks below the nozzle, the hydrodynamic resistance decreases along with the writing speed.

S10. Drawing lines on various substrates
The inks are printed on various substrates, including glass, plastics, aluminum, gold, and silicon wafer. As the surface property varies with the selection of materials, the height-to-width ratio depends on the materials. After thermal annealing, the surface profiles of EA and UA lines are measured on various substrates, from which the height-to-width ratio is measured as approximately 0.09, 0.08, 0.03, and 0.02 on glass, plastic, aluminum, and gold/silicon substrates for EA inks and 0.12, 0.10, 0.04, and 0.04 for the UA inks, respectively (fig. S23). The lines can be drawn even on the surface of paper although the excessive inks should be deposited to compensate for the infiltration into pores (fig. S24).

S11. Influence of fusion-induced shear force on crystallization
The faces, formed by fusion of lines, have a consistent orientation of fcc throughout the entire thickness, unlike lines. This is caused by the rearrangement of particles under a strong shear force during the fusion. The fusion occurs between a face and a newly drawn line, like a zip-up. The leading edge of fusion progresses at the rate of approximately 15 mm/s (fig. S25B and movie S5). To estimate the shear rate, the inks are instantly captured by photopolymerization during the middle of face printing, from which surface profiles are measured at three different positions of a) not fused yet, b) just fused, and c) fused sometime before (fig. S25C). The relative distances for the three positions of the profile measurement are converted to time intervals from the zip-up speed. That is, the position-dependent surface profile can be translated as the time-dependent surface profile at a fixed position. The shear rate is estimated as 6.27 s\(^{-1}\) for the first time interval of 0.13 s, which is 2.69 s\(^{-1}\) in the next interval of 0.34 s; the shear is estimated from by \(Ah^2r^1\) in the same manner as fig. S12. The shear rate is much greater than that in the spreading of single lines and comparable to that in the nozzle during the printing. It seems that the strong shear force triggers rearrange of particles along the fusion area and finally in the entire thickness to align (111) planes along the top and bottom surfaces of faces.

S12. Angle dependence of structural colors for direct-written faces
The high angle dependence of structural colors for the face made of EA ink is quantitatively studied by measuring reflectance spectra with various angles at the specular reflection and backward reflection conditions (fig. S26A to D). At the specular reflection condition, the reflectance peak shifts from 609 nm at 0 to 601 nm at 15°, 575 nm at 30°, and 535 nm at 45°. At the backward reflection, the directional specular reflection at stopband causes a dip in the spectra. Therefore, a dip appears at 601 nm at 15°, 584 nm at 30°, and 532 nm at 45°, which are consistent with the peak positions in the spectra at the specular reflection condition. The reflectance spectra are not measurable for the face made of UA ink at the specular reflection condition due to low reflectivity. Nevertheless, the spectra measured at the backward reflection condition show an almost invariable
peak position of 670 nm for various angles, indicating that the colloidal arrays are fully amorphous and isotropic form (fig. S26E). As an alternative way to compare angle dependence at the specular reflection, the faces are imaged at various angles (fig. S27). The face made of EA ink shows a large blue shift of structural colors, whereas that made of UA ink shows a relatively small blue shift, as shown in the photographs and CIE diagram.

S13. Influence of fusion on crystallization in non-optimal and optimal inks
The strong shear force by the fusion causes the crystallization of silica particles in UA inks with a volume fraction of $\phi = 0.20$ ($\sim \phi_{th}$). During the thermal annealing at 85°C, a stripe pattern appears along the direction of the line drawing in 10 min (fig. S28). The stripe pattern expands yet remains until 1 h. The reflectance peak appears and gets more pronounced during the annealing, reaching the reflectivity of 25%. The formation of long-range order is further confirmed with cross-sectional SEM images. Although crystalline structures can be produced by fusion-assisted rearrangement for faces with UA resin with $\phi - \phi_{th}$, the printability is not as good as EA and UA inks with optimum volume fraction.

For EA inks with optimum volume fraction, the fast fusion occurs from the third line when the lines are alternately drawn by displacing half the line width along the lateral direction. The second line is instantly fused during the drawing, which is much slower than the zip-up fusion. Therefore, thick lines formed by drawing two lines are not iridescent and show a square array along the top surface in the same manner as the single line (fig. S29). When a wide line is formed by the fusion of three lines, they show bright structural colors and high reflective intensity along the center (fig. S29, A to C), and hexagonal arrays are observed from the top surface near the center; square arrays are still observed from the top surface near the edges (fig. 29, D to J). As the line gets wider by merging more individual lines, the color becomes brighter and the area for the hexagonal arrays wider.

In contrast, EA inks with a low volume fraction show no zip-up. The low viscosity of the inks causes the fast and wide spreading of lines, which results in the merging of lines during the deposition not only for the second one but all. Therefore, there is no strong shear force to cause the rearrangement of particles, resulting in crystals with uncontrolled orientation. For example, the face drawn with the EA ink with $\phi = 0.30$ shows low maximum reflectivity of approximately 30% after annealing at 85°C for 1 h (fig. S30). The crystal orientations are not unified but somewhat random.

S14. Influence of carbon black nanoparticles on colloidal crystallization and optical property
Carbon black nanoparticles are additionally dispersed in the inks to enhance color chroma. As the carbon black nanoparticles absorb the entire range of the visible light, they can reduce incoherent scattering without altering the hue as long as they do not perturb the crystallization of silica particles. However, a large concentration of carbon black possibly interrupts the crystallization and causes too strong absorption of light. To find an optimum concentration, we disperse the carbon black nanoparticles at the concentrations of 0.05% w/w and 0.2% w/w in a silica-free resin basis and print faces, respectively. For the concentration of 0.05% w/w, the face displays enhanced color saturation in comparison with carbon black-free ink (figs. S31A and B). There is no reduction of reflectivity at the stopband position while the baseline is slightly lowered (fig. S31C). It is confirmed from the cross-section of the faces that the silica particles form a crystalline array in the presence of the carbon black nanoparticles at the concentration of 0.05% w/w (fig. S31D). The enhancement of color chroma with 0.05% w/w carbon black is also supported by CIE diagram
By contrast, the concentration of 0.2% w/w results in the dramatic drop of reflectivity (fig. S31C). Also, both color saturation and brightness are reduced (fig. S31, A and B). As confirmed from the cross-section, the crystallinity is significantly lowered with 0.2% w/w carbon black (fig. S31D). It seems that the reduction of crystallinity and strong absorption of the visible light at 0.2% w/w carbon black render the face dark and matte; it is noteworthy that transmittance is as low as approximately 10% for 120-μm-thick silica-free EA film containing 0.2% w/w carbon black whereas that is as high as approximately 60% for the film containing 0.05% w/w carbon black (fig. S31, F and G).

**S15. Unmixing and mixing at boundaries of two different inks**

When the same type of inks with different colors shares a boundary, low mobility of particles prevents the mixing at the boundary. For example, when two faces of red UA ink and blue UA ink are in contact, no blurring of boundary is observed at least for 4 days without photocuring (fig. S32A). There is no mixing between red EA ink and blue EA ink (fig. S32B). However, when EA and UA inks are in contact, a boundary gets blurred and new color stripes are formed (fig. S32C). There is a mixing of EA and UA in the boundary, which causes the local changes of the resin composition and particle volume fraction, resulting in undesired blurring and stripe formation. Therefore, the same type of inks should be used in the same positions for designing multicolor graphics with high precision.

**S16. Optical property of chromatic and achromatic colors**

Glittering and matte structural colors are developed by crystalline and amorphous arrays of colloidal particles with EA (PEA) and UA inks, respectively. The glittering faces made of EA inks show reflectance spectra featured as a pronounced single peak at stopband position whose reflectivity is higher than 80% and full width at half maximum (fwhm) is approximately 10 nm (fig. S33A). On the other hand, the matte faces made of UA inks show a broad peak whose height is approximately 8% and fwhm is approximately 45 nm (fig. S33D). CIE diagrams further support the difference between EA and UA inks (fig. S33, C and F). The achromatic colors of light brown and black are developed by light-absorbing polydopamine and carbon black nanoparticles, whereas the white is developed by incoherent scattering of silica particles with negligible structural resonance in the visible range. The polydopamine nanoparticles result in a gradual increase of reflectance along with the wavelength in the visible range, displaying a light brown (fig. S34). The carbon black nanoparticles make reflectance very low in the entire visible range, rendering the ink black. The scattering of large silica particles in the absence of any light-absorbing materials results in relatively high reflectance in the entire range, displaying white. The weight fractions of the additional nanoparticles are calculated with respect to UA weight.

**S17. Mechanical properties of direct-written faces**

To characterize mechanical properties, faces are printed with UA, EA, and PEA inks respectively and released to make free-standing films. The films are subjected to tensile and bending tests. In the tensile test with universal testing machine, Young’s modulus and strain at fracture are measured from the stress-strain curves (fig. S35A). The film made of UA ink shows Young’s modulus of 39.3 MPa and the strain at fracture of 0.51 so that it is tough and pliable. The film made of EA ink shows Young’s modulus of 243 MPa and the strain at fracture of 0.093, indicating that the material is rigid. The film made of PEA ink has Young’s modulus as small as 1.40 MPa and the strain at fracture of 0.67 so that it is elastic. In the bending test, the films are folded by
sandwiching them with two glass slides. The UA film remains intact for many times of folding as long as the radius of the curvature is not smaller than 0.2 mm (fig. S35B). When the radius of curvature decreases below 0.2 mm, the film is broken; the folded film is strongly compressed to achieve this small radius. By contrast, the EA film is broken when the radius of curvature decreases below 11.8 mm as it is brittle (fig. S35C). On the other hand, the PEA film is highly stretchable and foldable and it is impossible to break the film by folding.
Fig. S1.

**Threshold volume fraction for colloidal crystallization.** (A and B) Storage and loss modulus ($G'$ and $G''$) as a function of angular frequency for various volume fractions of silica particles dispersed in ethoxylated acrylate (EA) (A) and urethane acrylate (UA) (B), as denoted.
**Fig. S2.**

**Liquid-to-solid transition.** (A to C) Dispersions of silica particles with three different diameters of $d = 226$ nm, $190$ nm, and $175$ nm around the volume fraction responsible for liquid-to-solid transition in the resins of EA (A), PEA (B), and UA (C). Photo Credit: Jong Bin Kim, KAIST.
**Fig. S3.**

**Two distinct regions in the solvation layer.** (A) Cartoon for solvation layer composed of two regions: Inner region with strongly-bound molecules and outer region with loosely-bound molecules. (B) Crystalline array of particles produced by solvation-layer-induced interparticle repulsion. (C) Amorphous array of particles at the liquid-to-solid transition at which the inner regions of adjacent particles are brought into contact.
Fig. S4.
**Optimum volume fraction.** (A to C) Photograph and optical microscope images of pound signs drawn using EA inks with three different volume fractions of silica particles of 0.33 (A), 0.52 (B), and 0.535 (C). Photo Credit: Jong Bin Kim, KAIST.
Fig. S5.

**Volume-fraction dependence of colloidal arrangement.** (A and B) Cartoons showing the change of colloidal arrangement from a disordered state to crystalline and amorphous arrays along with the volume fraction of silica particles in EA or PEA (A) and UA (B). The threshold volume fractions for crystallization, $\phi_{th}$, are comparable for EA and UA, but the ranges for the crystal formation are different. In optimum volume fraction, $\phi_{opt}$ for printing, silica particles form a crystalline array for EA and an amorphous array for UA.
Fig. S6.

Angle dependence of structural colors for lines. (A) Illustration for specular reflection where the angle of incidence is the same as that of reflection. (B and C) Photographs of photonic lines printed with EA (B) and UA (C) inks taken at specular reflection condition with the denoted angles. (D and E) CIE diagram for structural colors from the photonic lines printed with EA (D) and UA (E) inks at various angles of specular reflection as denoted. Photo Credit: Jong Bin Kim, KAIST.
Fig. S7.

Shear-thinning and thixotropic relation for EA inks. (A) Viscosity of an EA ink with $\phi = \phi_{\text{opt}} = 0.51$ and $d = 190$ nm as a function of shear rate. (B) Temporal change of viscosity where the shear rate is abruptly increased from 0.01 s$^{-1}$ to denoted values at 180 s and returned to 0.01 s$^{-1}$ at 300 s.
Fig. S8.
Shear-thinning and thixotropic relation for UA inks. (A) Viscosity of a UA ink with $\phi = \phi_{\text{opt}} = 0.41$ and $d = 190$ nm as a function of shear rate. (B) Temporal change of viscosity where the shear rate is abruptly increased from 0.01 s$^{-1}$ to denoted values at 180 s and returned to 0.01 s$^{-1}$ at 300 s.
Fig. S9.

**Shear-dependent colloidal arrangement for EA inks.** (A) Storage and loss moduli of an EA ink with $\phi = \phi_{\text{opt}} = 0.51$ and $d = 190$ nm as a function of shear stress. (B) SEM image showing a string-like arrangement of silica particles in the EA ink that is photopolymerized immediately after the line printing. (C to E) Sets of schematics and corresponding cross-sectional SEM images showing the shear-dependent evolution of colloidal arrangement at three different states as denoted in (A). To take the cross-sectional images, the EA ink is sandwiched by a pair of two glass slides and sheared by moving the top slide to have strain rates of 0.01 s$^{-1}$ (C), 1 s$^{-1}$ (D), and 100 s$^{-1}$ (E).
Fig. S10.

Shear-dependent colloidal arrangement for UA ink. (A) Storage and loss moduli of a UA ink with $\phi = \phi_{\text{opt}} = 0.41$ and $d = 190$ nm as a function of shear stress. (B) Colloidal arrangement expected from A.
Fig. S11.
Spatial distribution of velocity in the gap. The velocity map is obtained from the superposition of parabolic Poiseuille flow and horizontal Couette flow for a typical printing condition.
Fig. S12.

Shear rate during lateral spreading of lines of EA inks. (A) Surface profile of lines at denoted times after the deposition and heat treatment. (B to D) Set of two profiles at denoted times for estimation of shear rate during the spreading. The yellow area is transferred into the green area during the time interval by spreading, from which shear rates are calculated for the initial 1.5 s (B), the next 2.5 s (C), and the next 3 s (D).
Fig. S13.
Shear rate by spreading of UA inks. (A) Surface profile of lines at denoted times after the deposition and heat treatment. (B to D) Set of two profiles at denoted times for estimation of shear rate during the spreading. The yellow area is transferred into the green area during the time interval by spreading, from which shear rates are calculated for the initial 3 s (B), the next 4 s (C), and the next 3 h (D).
Fig. S14.

**Square lattices in the top region of lines of EA inks.** (A) Illustration for various crystalline orientations in the cross-section of line. (B to D) Sets of observation plane (a), lattice structure (b), and SEM images (c and d) showing colloidal arrays in the top region of lines: top surface (B), normal cross-section (C), and oblique cross-section at the angle of 45° (D), where [200] and [220] directions are denoted. The writing direction is denoted in B. Two SEM images are taken at two different lateral positions as marked in A.
Fig. S15.
String-like arrangement in the middle region of lines of EA inks. (A) Illustration for various crystalline orientations in the cross-section of line. (B to D) Observation plane of normal cross-section (B), lattice structure (C), and SEM images (D) showing the vertical alignment of string-like [200] direction of fcc lattice in the middle region of lines. The positions at which SEM images are marked in A.
Fig. S16.
Normal alignment near the bottom surface of lines of EA inks. (A) Illustration for various crystalline orientations in the cross-section of line. (B to D) Observation plane of normal cross-section (B), lattice structure (C), and SEM images (D) showing the vertical alignment of [111] direction of fcc lattice in the bottom region of lines. The positions at which SEM images are marked in A.
Fig. S17.
Relative thickness of each domain in lines of EA inks. (A) Illustration for various crystalline orientations in the cross-section of line. (B) Low magnification SEM image showing the entire cross-section. (C to E) SEM images showing the boundary between top and middle regions (C) and the boundary between middle and bottom regions (D and E). The positions at which SEM images are marked in A and B.
Fig. S18.

Optical properties of lines printed with EA ink. (A to C) Illustration for reflection from the central area of a line (A), corresponding reflectance spectrum (B), and OM images (C). (D to F) Same sets with A to C for the side area. The reflectance spectrum from the central area has two peaks corresponding to (111) planes and (200) planes of a fcc lattice, whereas that from the side area has one peak from (111) planes, as expected from the cross-section in Fig. 1.
Fig. S19.

Amorphous array in the entire volume of lines of EA inks. (A) Illustration for amorphous array in the entire cross-section. (B) Observation plane of normal cross-section. (C) SEM images showing amorphous arrays taken at two different positions as marked in A.
Fig. S20.

Optical properties of lines printed with UA ink. (A and B) Reflectance spectrum (A) and OM image (B) taken from the central area of the line printed with UA ink.
Fig. S21.
Condition for drawing lines with a consistent width. (A) Illustration for the nozzle shape and dimensions. (B) Snapshot photograph showing the formation of a straight line for an EA ink with a pneumatic pressure of 100 kPa, writing speed of 10 mm/s, and a gap distance of 50 μm. (C) Photograph showing the formation of a wavy line with a pneumatic pressure of 100 kPa, writing speed of 10 mm/s, and a gap distance of 200 μm. (D) Photograph showing the formation of dots with a pneumatic pressure of 100 kPa, writing speed of 20 mm/s, and a gap distance of 200 μm.
Fig. S22.

Influence of printing parameters on flow rate. (A and B) Volumetric flow rate as a function of pneumatic pressure for EA inks (A) and UA ink (B). The gap distance is set to 100 μm and the writing speed is set to 1 mm/s. (C and D) Volumetric flow rate as a function of writing speed for various gap distances and pneumatic pressures for EA inks (C) and UA ink (D).
Fig. S23.
Surface profiles of lines on various substrates. (A and B) Lines of EA inks (A) and UA inks (B) on the surfaces of the glass (a), acryl film (b), aluminum (c), gold (d), and silicon wafer (e) after thermal annealing.
Fig. S24.

Deposition on papers. Cross-sectional SEM image showing EA inks deposited on a paper where the EA ink is overdosed to make a photonic layer over the ink-absorbing paper.
Shear rate during the fusion. (A) Illustration for drawing a face by fusion of lines. (B) Series of snapshot photographs showing the progress of the leading edge of fusion. The time interval between (1) and (2) is 0.3 s and that between (2) and (3) is 0.17 s. The leading edges are denoted with arrows. (C) Photograph of instantly captured faces during the printing at which surface profiles at denoted positions are measured: Not yet fused (a), just fused (b), and fused sometime before (c). (D and E) Surface profiles measured from C, where time intervals are denoted from the distances between the measurements by considering the progress rate of the leading edge of fusion. The yellow area is transferred into the green area for the time interval by the fusion. Photo Credit: Jong Bin Kim, KAIST.
Fig. S26.

Angle dependence of reflectance spectra for faces. (A) Illustration for specular reflection. (B) Reflectance spectra of the face printed with EA ink at the specular reflection at denoted angles. (C) Illustration for backward reflection. (D and E) Reflectance spectra of the faces printed with EA (D) and UA (E) inks at the backward reflection at denoted angles. The dips are denoted with arrows in (D).
Fig. S27.
**Angle dependence of structural colors for faces.** (A) Illustration for specular reflection. (B and C) Photographs of faces printed with EA (B) and UA (C) inks taken at specular reflection condition with the denoted angles. (D and E) CIE diagram for structural colors from the faces printed with EA (D) and UA (E) inks at various angles of specular reflection as denoted. Photo Credit: Jong Bin Kim, KAIST.
Fig. S28. 

Crystallization for a face of UA ink with threshold volume fraction. (A and B) Evolution of reflectance spectrum (A) and color (B) during thermal annealing of a face drawn using a UA ink with a particle diameter of 145 nm and volume fraction of 0.20 at 85°C, where OM images (top panels) and photographs (bottom panels) are shown in (B). (C and D) Cross-sectional SEM images of the faces immediately cured (C) and cured after thermal annealing for 1 h (D). Photo Credit: Jong Bin Kim, KAIST.
Fig. S29.
**Fusion-induced rearrangement.** (A to C) Photographs (A), OM images (B), and reflectance spectra (C) of lines with various widths produced by drawing single or multiple lines as denoted, where the spectra are measured from topmost region. The lines are drawn with a pitch of 300 µm. (D) Illustration of top-surface observation. (E and F) Lattice structures of (111) plane (E) and (200) plane (F). (G to J) SEM images of the top surfaces taken at two different positions near the center and edge as denoted for a single line (G) and wider lines formed by drawing two, three, and four lines (H to J). Photo Credit: Jong Bin Kim, KAIST.
Fig. S30.

**Uncontrolled orientation of crystals without zip-up fusion.** (A and B) Evolution of reflectance spectrum (A) and color (B) during thermal annealing of a face drawn using an EA ink with a particle diameter of 145 nm and volume fraction of 0.30 at 85°C, where OM images (top panels) and photographs (bottom panels) are shown in (B). (C and D) Cross-sectional SEM images of the faces immediately cured (C) and cured after thermal annealing for 1 h (D). Photo Credit: Jong Bin Kim, KAIST.
Fig. S31.

Effect of the concentration of carbon black nanoparticles. (A to C) Photographs (A), OM images (B), and reflectance spectra (C) of the faces printed with EA inks containing carbon black nanoparticles at the concentrations of 0, 0.05, and 0.2% w/w. (D) Cross-sectional SEM images of the films with three different concentrations of carbon black. (E) CIE diagram for the colors of the films with carbon black nanoparticles of 0 and 0.05% w/w. (F and G) OM images at transmission mode (F) and transmittance spectra (G) of 120-μm-thick films made from silica-free EA containing carbon black nanoparticles at three different concentrations. Photo Credit: Jong Bin Kim, KAIST.
Fig. S32.

Mixing between EA and UA inks. (A to C) Photographs of uncured faces composed of two different inks: Red UA and blue UA inks (A), red EA and blue EA inks (B), and blue UA and red EA inks (C). The faces are incubated at room temperature at denoted times. The boundaries in the UA-UA face and EA-EA face remain unblurred for 4 days, whereas that in the UA-EA face is blurred and color-changed. Photo Credit: Jong Bin Kim, KAIST.
Fig. S33.

**RGB colors from direct-written photonic faces.** (A to C) Reflectance spectra (A), OM images (B), and CIE diagram (C) for blue-, green-, and red-colored faces printed with EA inks, where silica particles with a diameter of 175 nm at 50% v/v, 190 nm at 51% v/v, and 226 nm at 52% v/v are used respectively. (D to F) Same sets with (A to C) for the faces printed with UA inks, where 145 nm at 38% v/v, 190 nm at 41% v/v, and 226 nm at 43% v/v are used, respectively.
Fig. S34.
Achromatic colors from direct-written faces. (A and B) Reflectance spectra (A) and OM images (B) for white, light brown, and black faces printed using UA inks.
Fig. S35.

**Mechanical properties of the printed films.** (A) Tensile stress-strain curves for faces printed with EA, UA, and PEA inks. (B and C) Cross-sectional OM images of folded films immediately before the fracturing for UA (B) and EA (C) inks.
Legends for Movies S1 to S10

Movie S1.
Direct writing of an Eiffel tower with blue UA ink. The Eiffel tower is drawn with UA ink with 145-nm-diameter silica particles and volume fraction of 0.40 at the writing speed of 8 mm/s on a glass substrate with the gap between the nozzle and substrate of 100 μm.

Movie S2.
Comparison of iridescence for the Eiffel tower with crystalline and amorphous arrays. The Eiffel tower pattern printed using EA ink is strongly iridescent whereas that using UA ink is less iridescent.

Movie S3.
Direct writing of “Happy Birthday” in cursive script with green UA ink. The trajectory is compartmentalized into multiple segments with five corresponding writing speeds of 0.8, 1.5, 2.5, 4, and 7 mm/s for targeting line widths, where UA ink with 190-nm-diameter silica particles and volume fraction of 0.41 is used.

Movie S4.
Comparison of iridescence for “Happy Birthday” in cursive script with crystalline and amorphous arrays. The “Happy Birthday” pattern printed using EA ink is strongly iridescent whereas that using UA ink is less iridescent.

Movie S5.
Zip-up fusion during face printing. EA ink with 226-nm-diameter silica particles and volume fraction of 0.52 is direct-written at 3 mm/s with the gap between the nozzle and substrate of 100 μm, where spacing between two adjacent lines is set to 300 μm. The leading edge of fusion progresses at the speed of approximately 15 mm/s.

Movie S6.
Reflection and transmission for a Marilyn Monroe drawn using EA ink. Marilyn Monroe is printed on a glass substrate using EA ink with 226-nm-diameter silica particles and volume fraction of 0.52, which is illuminated with white light while adjusting the angle of incidence. The reflection and transmission colors vary with the angle.

Movie S7.
Comparison of iridescence for rose & leaves with crystalline and amorphous arrays. The rose & leaves pattern printed using EA inks is strongly iridescent whereas that using UA inks is less iridescent.

Movie S8.
Direct writing of Mickey Mouse with various inks. The Mickey Mouse is drawn using five different inks which are light brown and white UA inks and black, red, and green EA inks.
Movie S9.

Comparison of iridescence for the crystalline and amorphous arrays in the Golden Gate Bridge pattern. The bridge printed using EA inks is strongly iridescent whereas the river printed using UA ink is less iridescent. The gulls and the footstone of bridge are printed using white and black UA inks.

Movie S10.

Mechanochromic chameleon drawn using PEA inks. The chameleon is printed on glass substrate using PEA inks, which is transferred on an elastomer film to show mechanochromic property.