# Supporting Information

# Wide Gamut Biomimetic Structural Colors from Interference Assisted Two-Photon Polymerization

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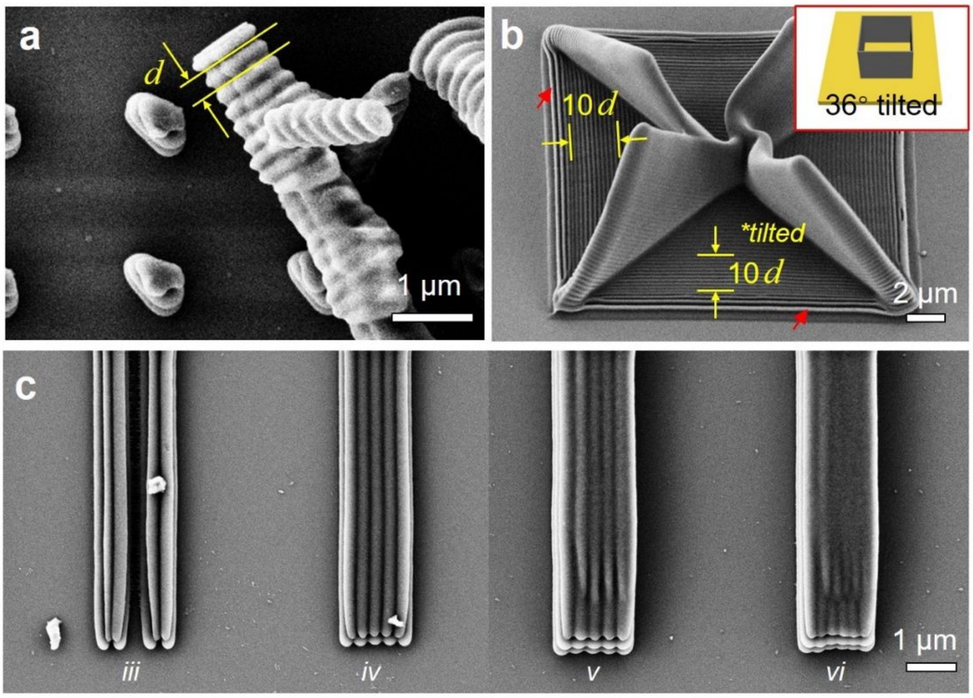


**Figure S1**. SEM images of various structures printed by the interference-assisted TPP technique. (a) Top view of an array of voxels with multilayer structures, of which some were tilted or collapsed. (b) Oblique view (~36° tilted) of a collapsed box frame with multilayer structures, top right corner is the scheme of a 20 × 20 × 12 μm$^3$ box. *d* denotes the distance between two adjoining layers. Red arrows indicate the separation of layers. (c) Top view of parallel laser scanning paths with various line distances, corresponding to schemes *iii*-*vi* in Figure S2.

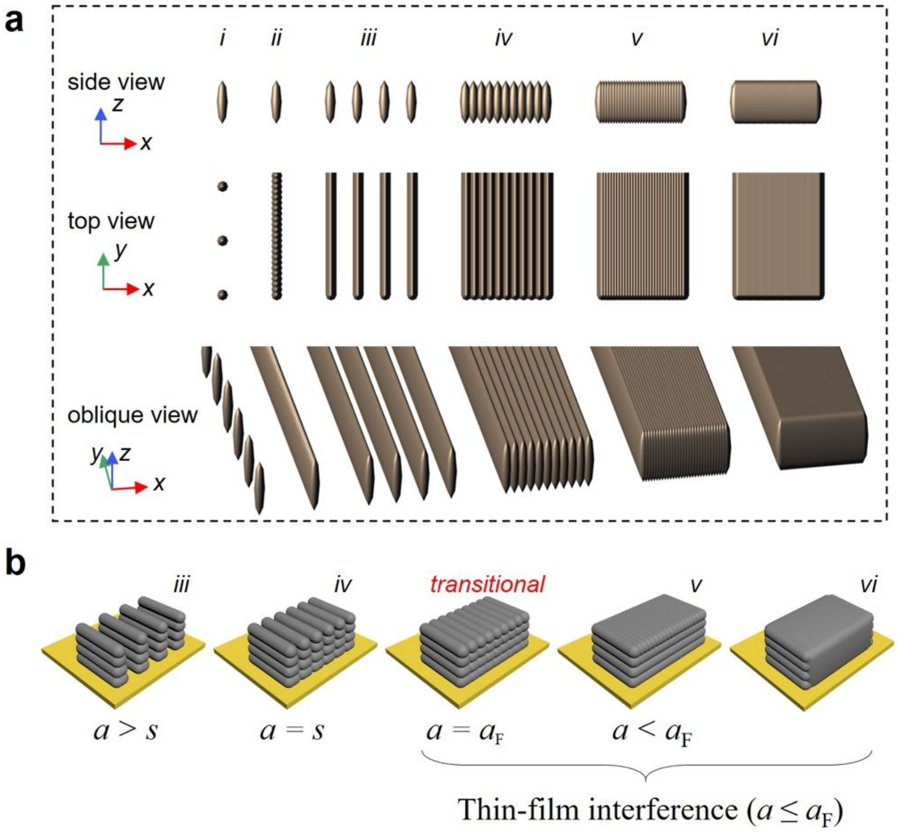


**Figure S2**. Schematic illustration of laser scanning trajectories (a) and the polymerized multilayer structures (b). The femtosecond laser works in pulse mode (*i* and *ii*) at low (*i*) and high (*ii*) repeat rates, or in continuous mode (*iii*-*vi*), which turns the sequential voxels into continuous lines (*iii*) or even a block (*vi*) as the line distance decreases gradually.

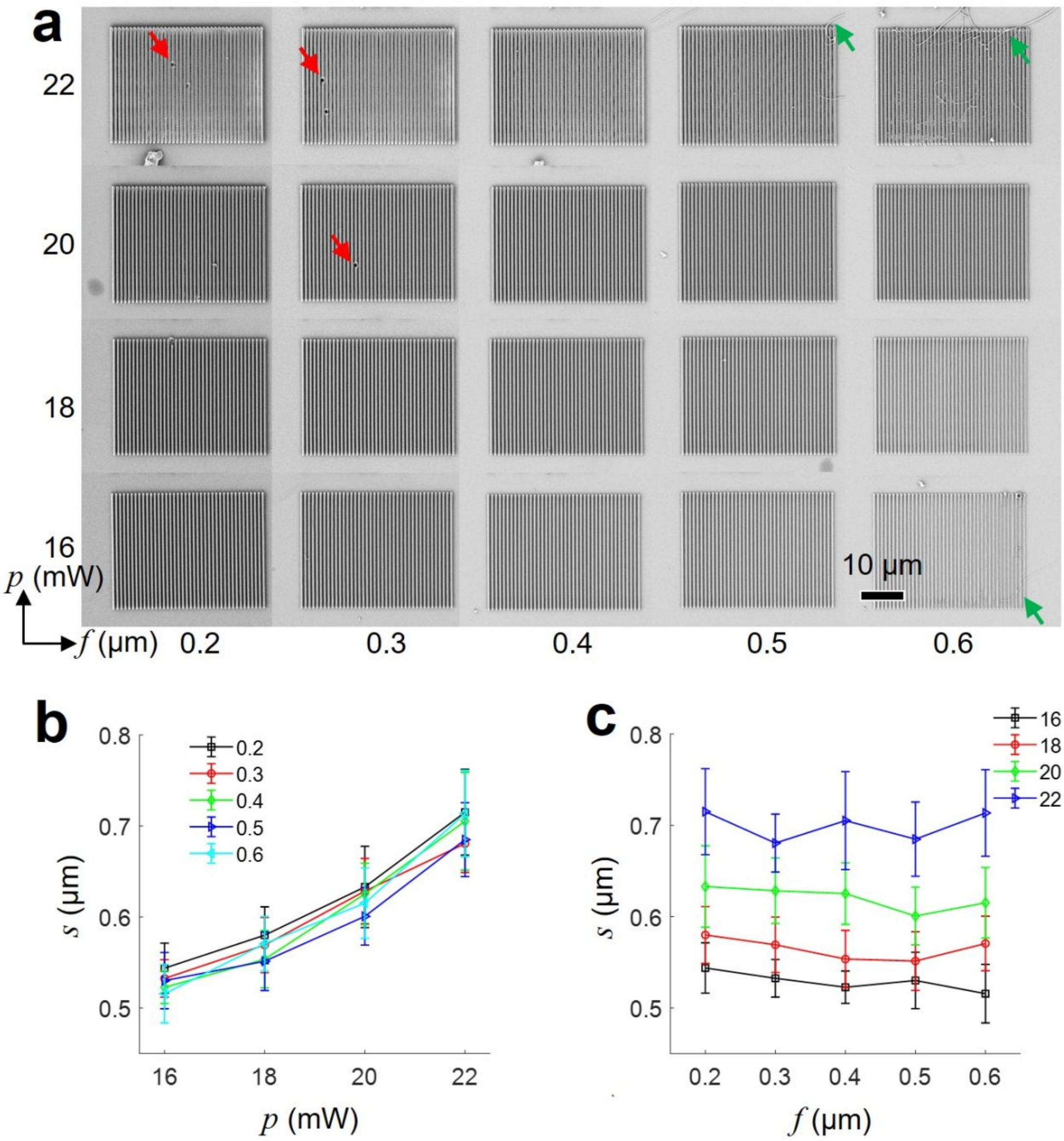


**Figure S3**. SEM images of BSC pixels (a) and the relationship between the feature size and the laser power (b) or the focus depth (c). Each feature size was measured 10 times and averaged. The red arrows indicate the accumulated heat-induced explosions, and the green arrows indicate the layer separations.

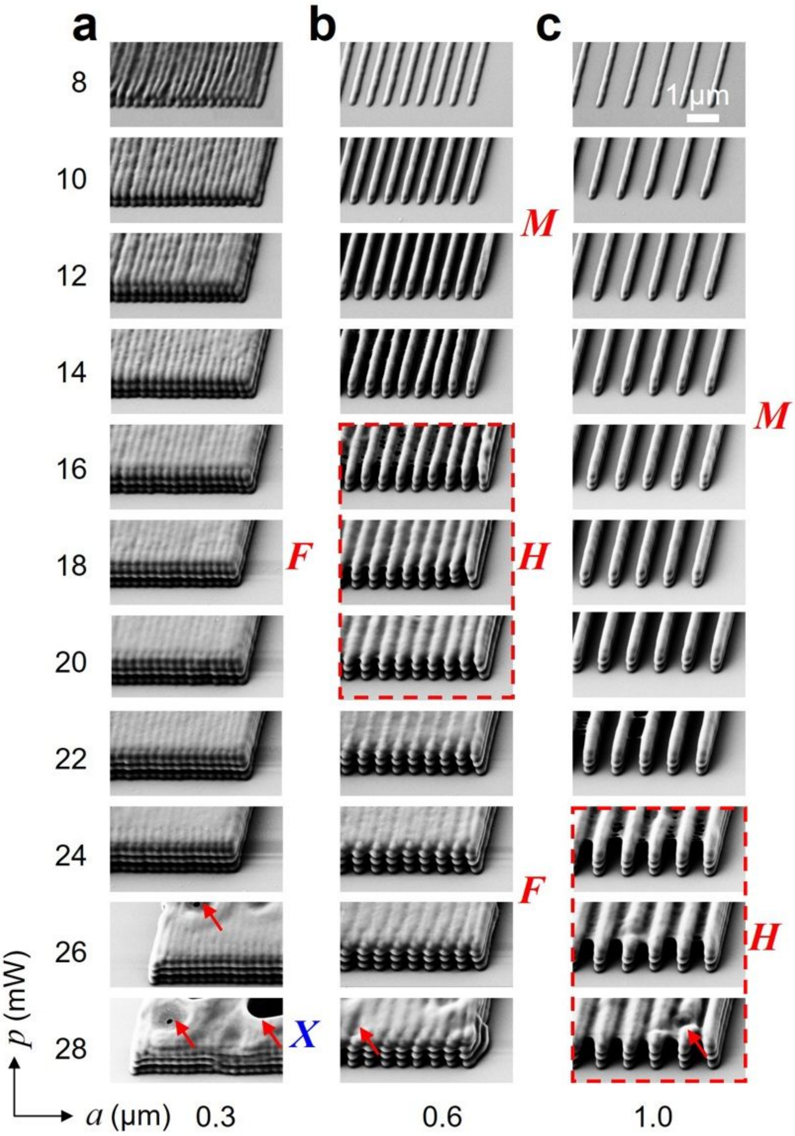


**Figure S4**. (a-c) SEM images of three columns of BSC pixels with CVPs (0.3, *p*, 0.0, 3000) (a), (0.6, *p*, 0.0, 3000) (b) and (1.0, *p*, 0.0, 3000) (c). The laser power increased from 8 mW to 28 mW in steps of 2 mW for each column. Red arrows indicate the photoresist explosions. *M*: multilayer interference, *H*: hybrid, *F*: thin-film interference, *X*: explosions.

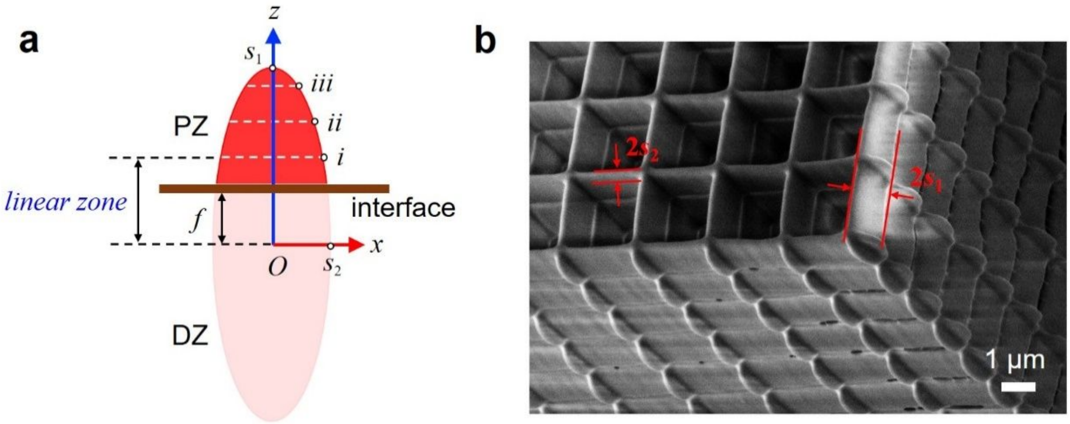


**Figure S5**. The aspect ratio of a TPP voxel. (a) Schematic illustration of a voxel with the aspect ratio of 3. The horizontal intercept (lateral feature size $s$) decreases gradually to the focus depth $f$. ($i$) $s = 0.866\times(2s_2)$ at $f = 0.5\ s_1$; ($ii$) $s = 0.715\times(2s_2)$ at $f = 0.7\ s_1$; ($iii$) $s = 0.436\times(2s_2)$ at $f = 0.9\ s_1$. (b) SEM image of a woodpile structure with the aspect ratio ($s_1/s_2$) of ~3.

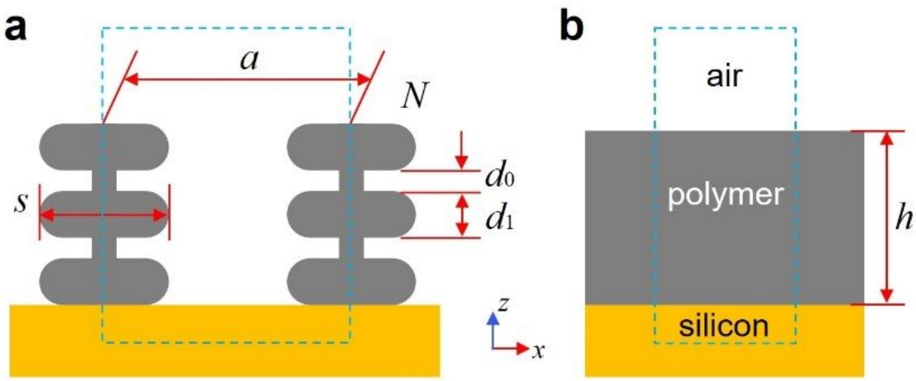


**Figure S6**. Geometrical configurations of the multilayer interference (a) and the thin-film interference (b) for the FDTD simulation. The dotted blue squares indicate the simulation regions. Default values for the parameters are: $N = 3$, $a = 1000$ nm, $s = 300$ nm, $d_1 = 200$ nm, $h = 200$ nm. $d_0 + d_1 = 256.6$ nm was constant.

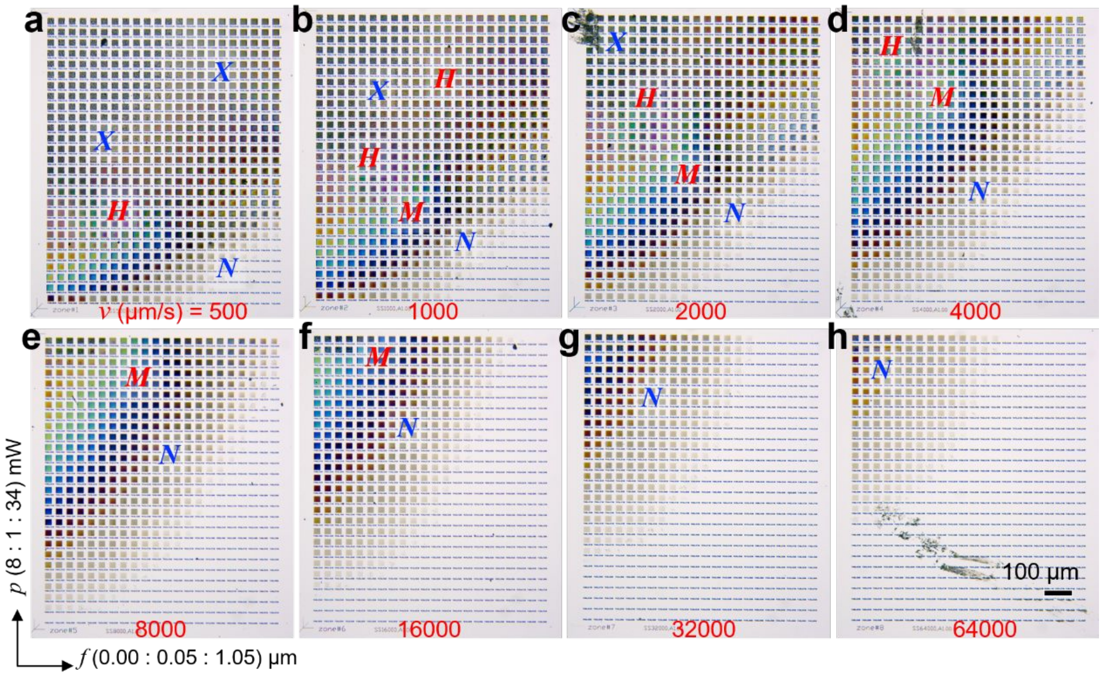


**Figure S7**. (a-h) Optical microscope images of eight *v*-*p*-*f* palettes printed by using CVP (1.0, *p*, *f*, *v*) and three parameter sweeps: (1) *v* increased from 500 μm $s^{-1}$ to 6400 μm $s^{-1}$ as a geometric series with a constant ratio of 2 for (a-h); (2) *p*(8 : 1 : 34) (unit: mW) along the *y*-direction within each palette; (3) *f*(0.00 : 0.05 : 1.05) (unit: μm) along the *x*-direction within each palette. *a* = 1.0 μm was constant. The size of each pixel is 25 × 25 $\mu m^2$. *M*: multilayer interference, *H*: hybrid, *X*: explosions, *N*: null.

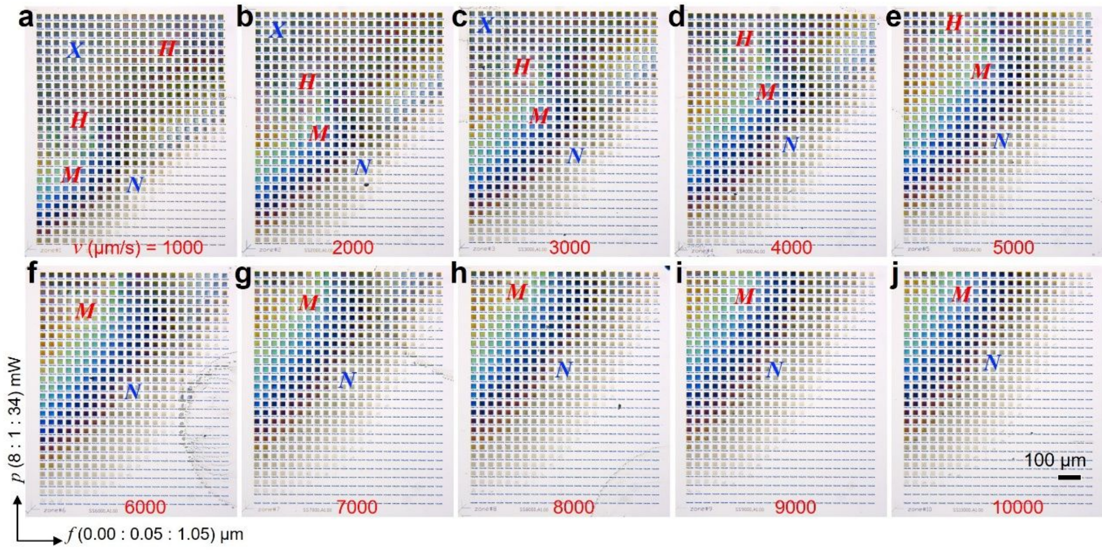


**Figure S8**. (a-j) Optical microscope images of ten *v*-*p*-*f* palettes printed by using CVP (1.0, *p*, *f*, *v*) and three parameter sweeps: (1) *v*(1000 : 1000 : 10000) (unit: μm $s^{-1}$) for (a-j); (2) *p*(8 : 1 : 34) (unit: mW) along the *y* direction within each palette; (3) *f*(0.00 : 0.05 : 1.05) (unit: μm) along the *x* direction within each palette. *a* = 1.0 μm was constant. The size of each pixel is 25 × 25 $\mu m^2$. *M*: multilayer interference, *H*: hybrid, *X*: explosions, *N*: null.

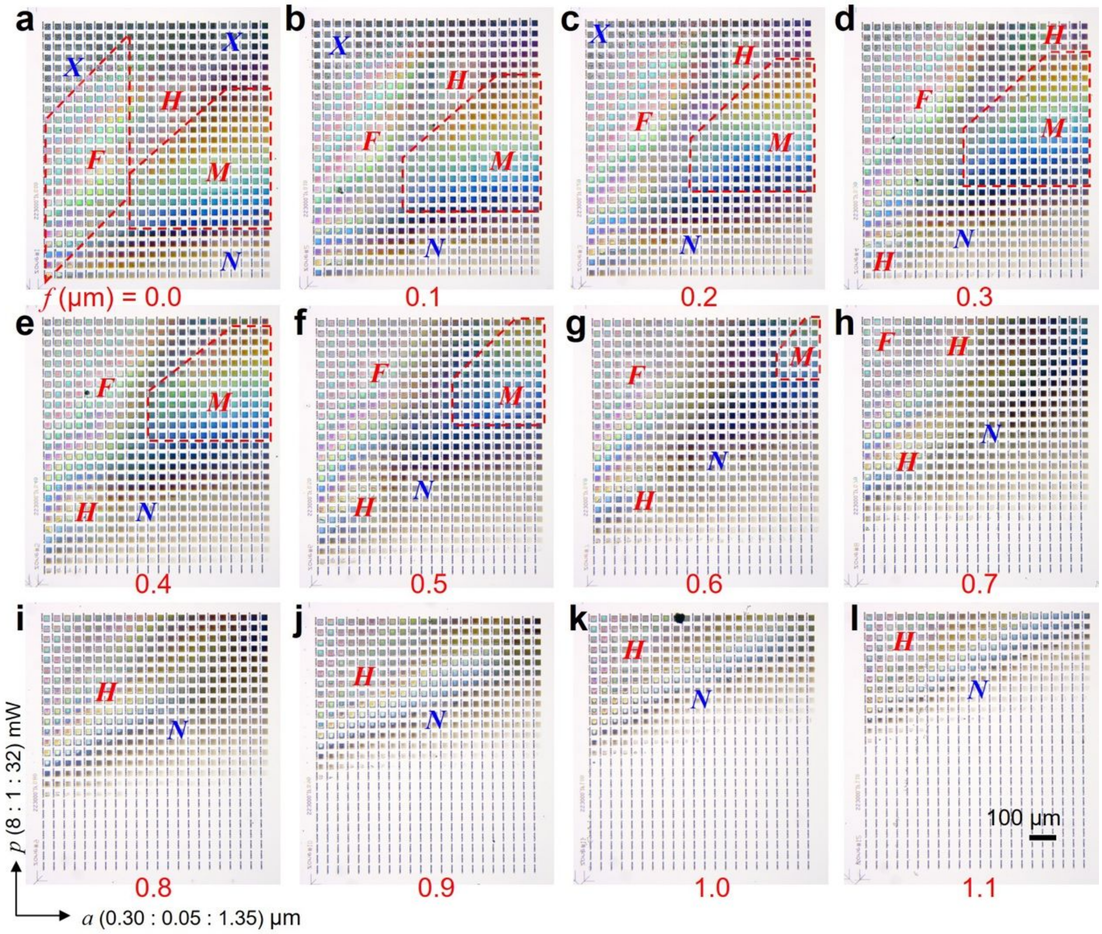


**Figure S9**. (a-l) Optical microscope images of twelve *f*-*p*-*a* palettes printed by using CVP ($a$, $p$, $f$, 3000) and three parameter sweeps: (1) $f$(0.0 : 0.1 : 1.1) (unit: μm) for (a-l); (2) $p$(8 : 1 : 32) (unit: mW) along the $y$ direction within each palette; (3) $a$(0.30 : 0.05 : 1.35) (unit: μm) along the $x$ direction within each palette. $v$ = 3000 μm $^{-1}$ was constant. The size of each pixel is 25 × 25 μm$^2$. *M*: multilayer interference, *H*: hybrid, *F*: thin-film interference, *X*: explosions, *N*: null.

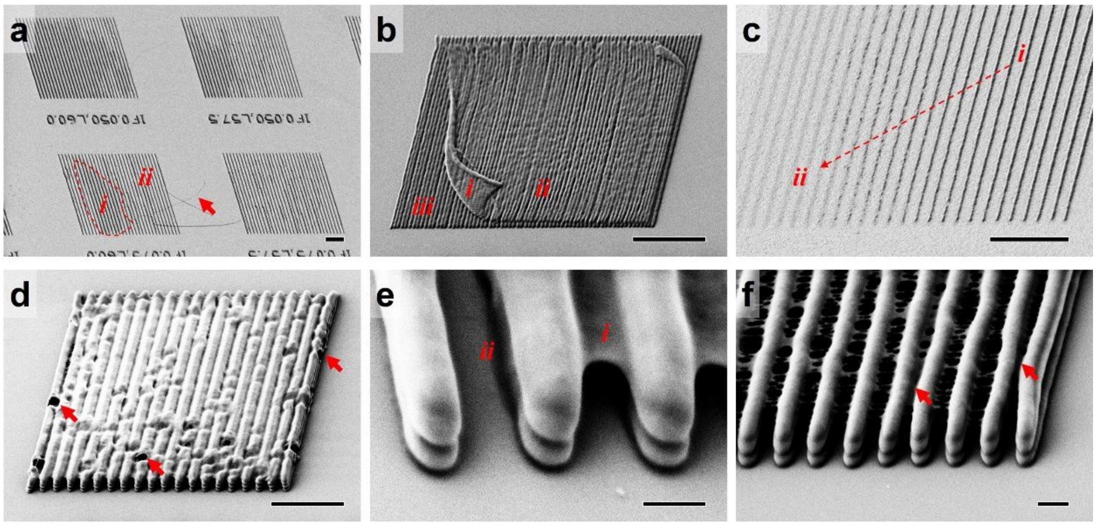


**Figure S10**. SEM images of BSC pixels with various defects. (a) Layer separations. Top layers were partially or entirely peeled off and collapsed (*i*), overlapped (*ii*), and detached (*iii*). (b) Top layer was partially folded, and thus $h_{iii} < h_{ii} < h_i$ (*h* denotes the overall thickness). (c) The substrate was slightly tilted and thus made gradient focus depths along the *i*-*ii* direction. (d) The polymer layers exploded due to the accumulated heat effect under high laser powers. (e) Overhangs or accessories occurred between two adjoining lines (*i* was occupied, while *ii* was still clear). (f) The polymer lines were partially twisted, the arrows pointed to the narrower parts. Scale bars are 5 µm in (a-d) and 500 nm in (e, f).

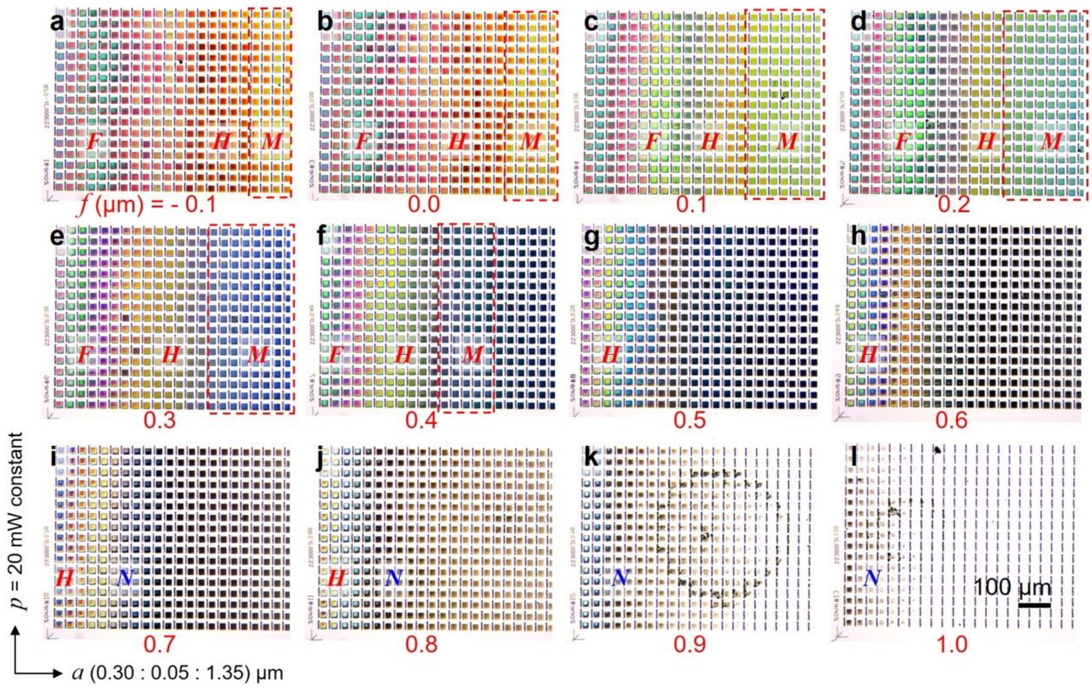


**Figure S11**. (a-l) Optical microscope images of twelve *f*-*p*-*a* palettes printed by using CVP (*a*, 20, *f*, 3000) and two parameter sweeps of *f*(-0.1 : 0.1 : 1.0) (unit: μm) for (a-l) and *a*(0.30 : 0.05 : 1.35) (unit: μm) along the *x* direction within each palette. $p = 20$ mW and $v = 3000$ μm $s^{-1}$ were constant. The size of each pixel is 25 × 25 $\mu m^2$. *M*: multilayer interference, *H*: hybrid, *F*: thin-film interference, *N*: null.

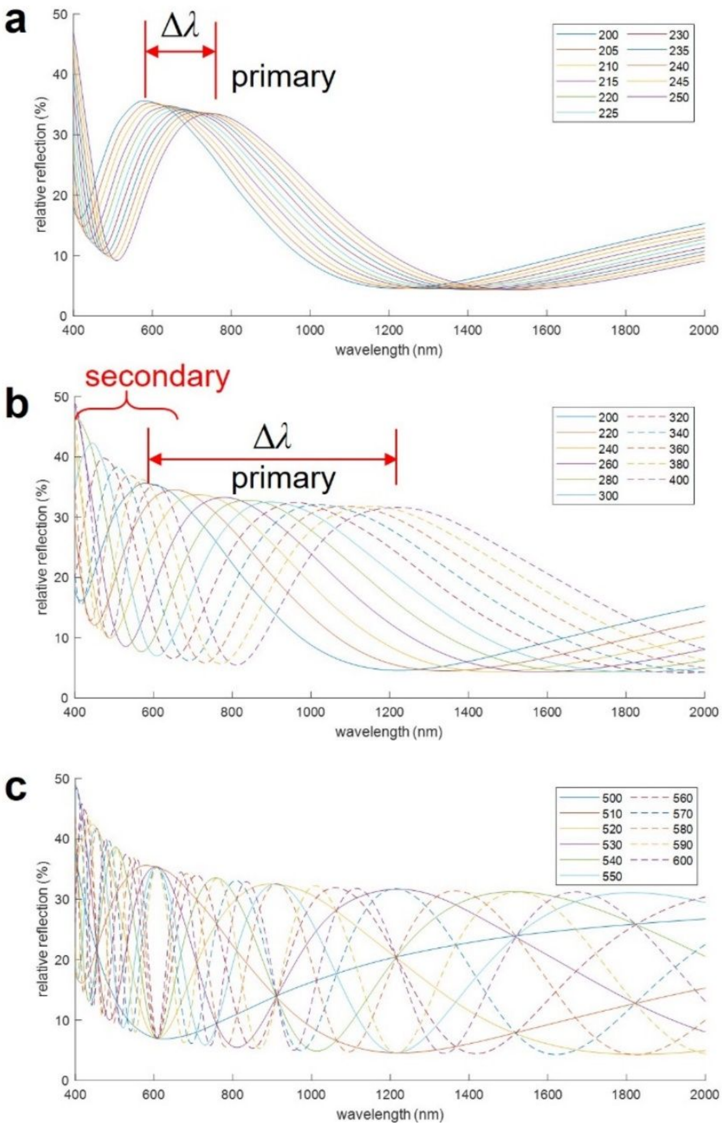


**Figure S12**. Simulated reflection spectra of a thin film with various thickness: (a) $h$(200 : 5 : 150) (unit: μm); (b) $h$(200 : 20 : 400) (unit: μm); (c) $h$(500 : 10 : 600) (unit: μm).

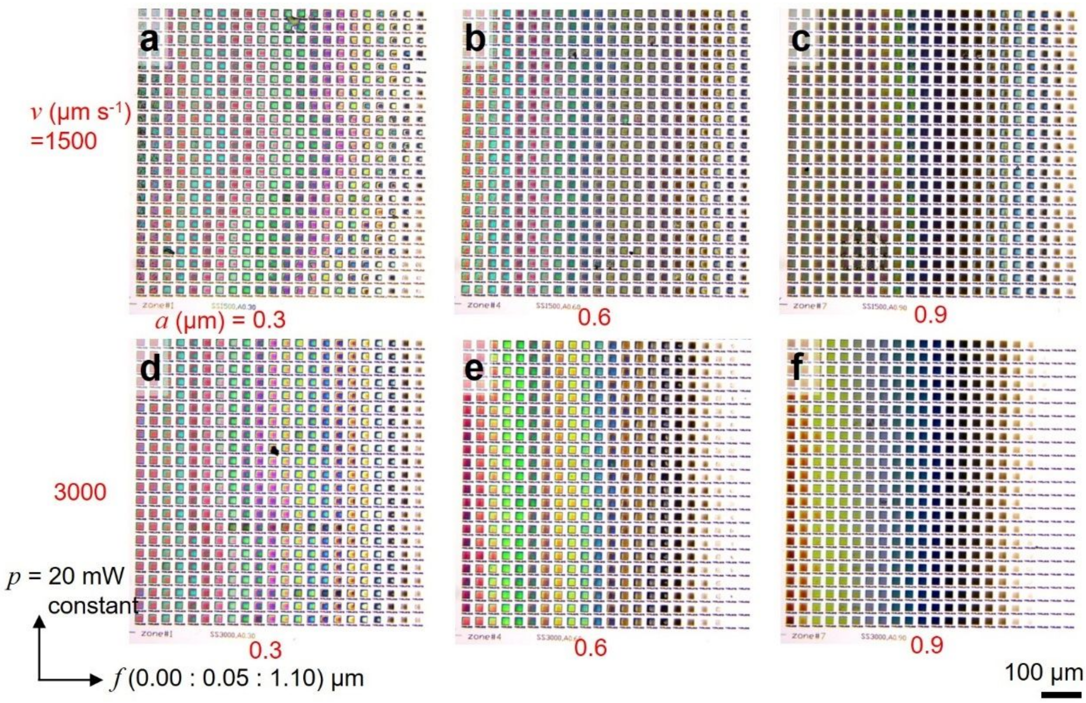


**Figure S13**. (a-f) Optical microscope images of six *a*-*v*-*f* palettes printed by using CVP (*a*, 20, *f*, *v*) and three parameter sweeps: (1) *a*(0.3 : 0.3 : 0.9) (unit: µm) for (a-c) and (d-f), respectively; (2) *v*(1500 : 1500 : 3000) (unit: µm $s^{-1}$) for the upper and the lower rows, respectively; (3) *f*(0.00 : 0.05 : 1.10) (unit: µm) along the *x* direction within each palette. *p* = 20 mW was constant. The size of each pixel is 25 × 25 µm$^2$.

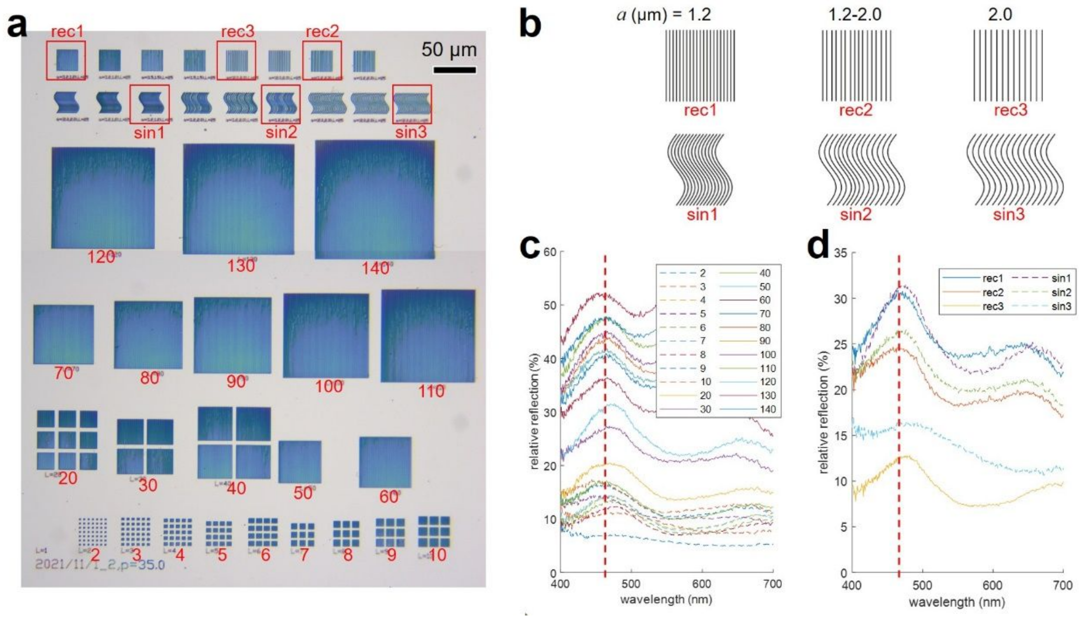


**Figure S14**. Optical microscope (20X objective) images and the corresponding reflection spectra of various BSC pixels. (a) All pixels were printed with CVP (*a*, 20, 0.0, 3000). First row, rectangle pixels with various line distance: *a* = 1.2 μm for rec1, *a* = 1.2-2.0 μm (random) for rec2, and *a* = 2.0 μm for rec3; second row, *sine*-shape pixels with various line distance: *a* = 1.2 μm for sin1, *a* = 1.2-2.0 μm (random) for sin2, and *a* = 2.0 μm for sin3; the rest were typical pixels (*a* = 1.0 μm) with various side lengths (*L* = 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 μm). (b) Scanning trajectories for the rectangle and the *sine*-shape pixels, the line distances of rec2 and sin2 were random numbers between 1.2 and 2.0 (unit: μm). (c, d) Reflection spectra of the typical (c), the rectangle, and the *sine*-shape pixels (d).

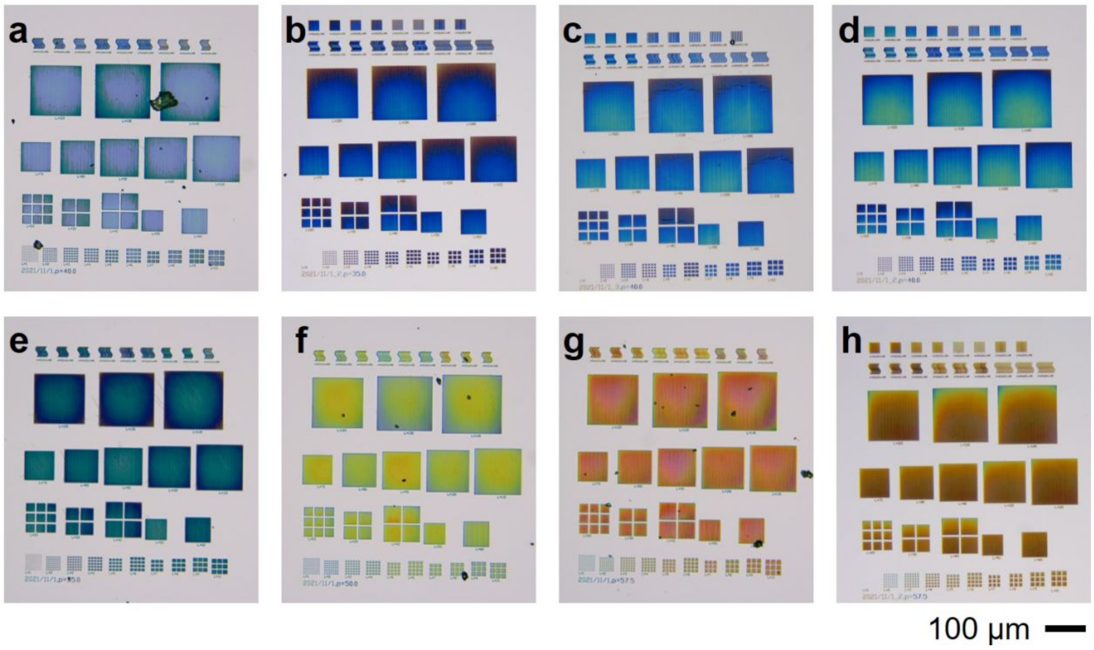


**Figure S15**. (a-h) Optical microscope (10X objective) images of eight groups of BSC pixels with various CVPs. (b) was enlarged in Figure S14a by using a 20X objective.

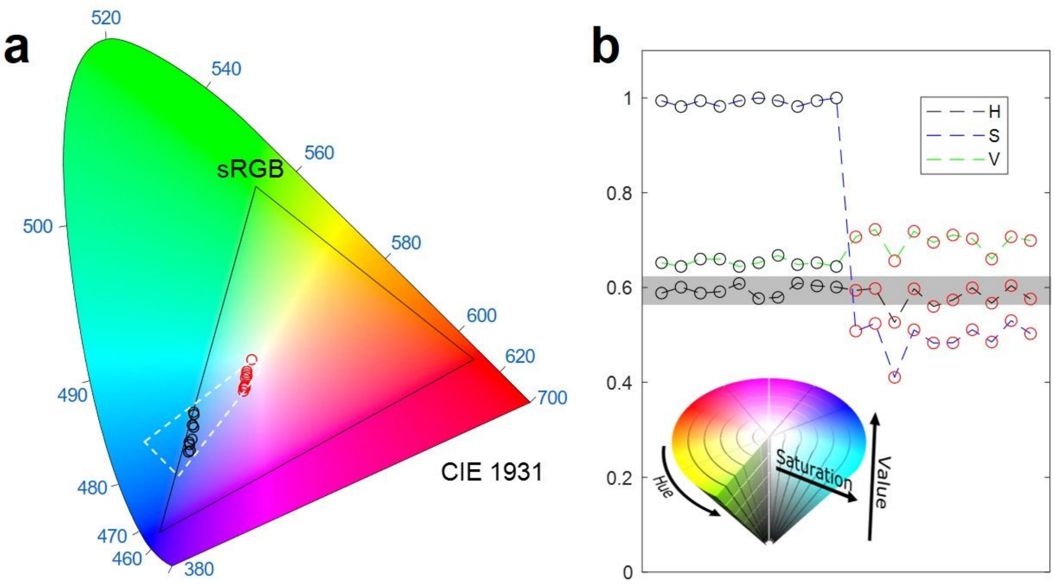


**Figure S16**. The color distribution of 20 selected BSC pixels from Figure S14a (10 pixels, red circles) and Figure S15b (10 pixels, black circles) in the CIE 1931 chromaticity diagram (a) and the HSV color space (b).


**Figure S17**. Optical microscope images of four groups of *butterfly*-shape pixels fabricated by using CVP ($a$, $p$, $f$, 3000) and three parameter sweeps: (1) $f$(0.0 : 0.1 : 0.3) (unit: μm) for these groups; (2) $p$(16 : 1 : 32) (unit: mW) along the $y$ direction within each group; (3) $a$(0.5 : 0.1 : 1.0) (unit: μm) along the $x$ direction within each group. $v$ = 3000 μm $^{-1}$ was constant. Each *butterfly*-shape pixel is 70 × 50 μm$^2$.

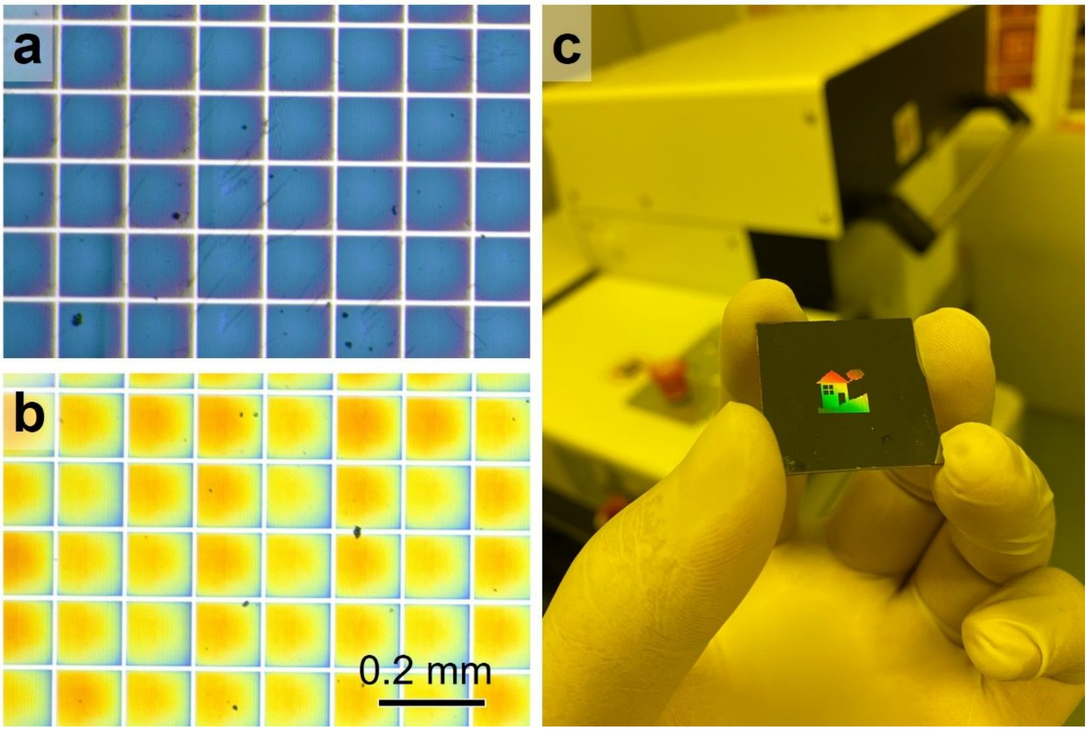


**Figure S18**. The art painting of *cabin-in-hillside* with bigger pixels ($L$ = 140 μm). (a, b) Optical microscope images of the blue (a) and yellow (b) pixels. (c) The researcher held an as-fabricated art painting on a 2.5 × 2.5 cm$^2$ silicon in front of the TPP system.

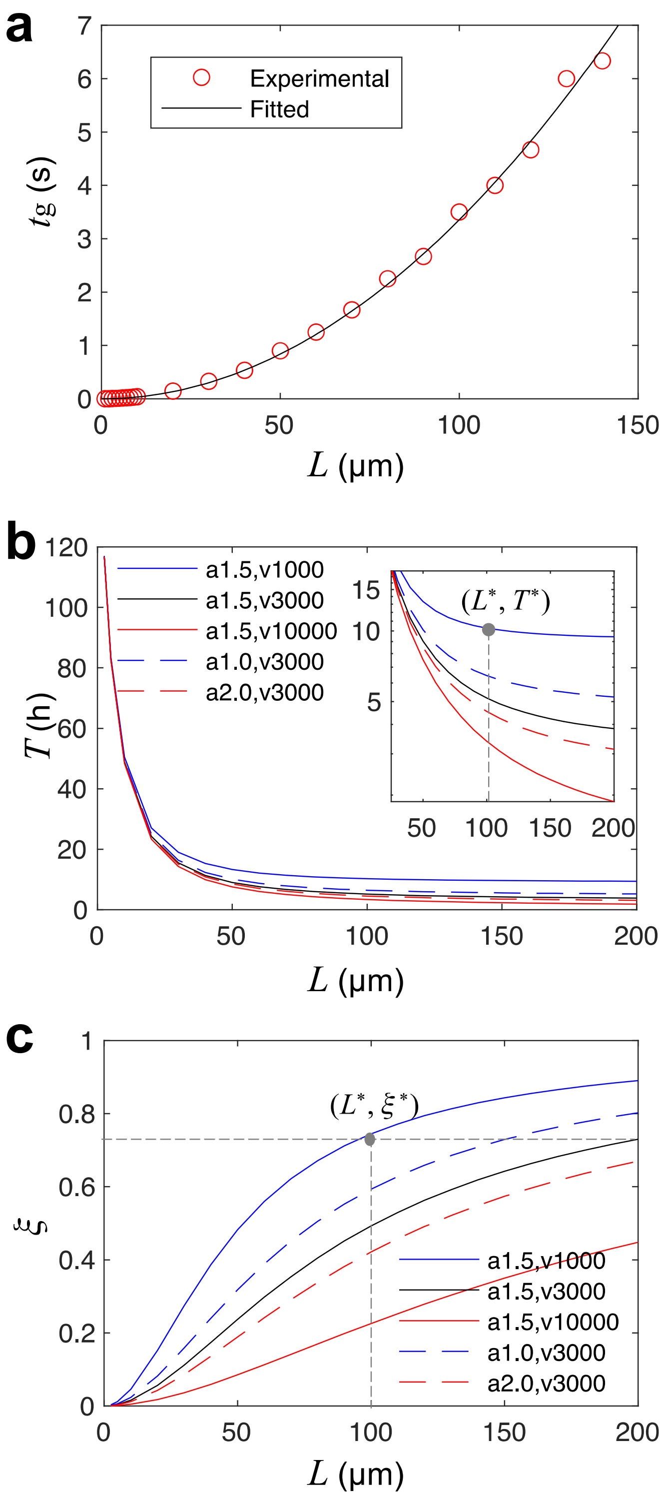


**Figure S19**. Calculation of the time cost and the related time efficiency of a single BSC pixel (a) or an art painting (b, c) by using pixels with various side lengths. (a) Time cost on a single pixel with constant CVP (1.0, 20, 0.0, 3000) but various $L$ (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 μm). The circles and the line were experimental data and fitted curve, respectively. (b) Five groups of the calculated time cost on a 1 $cm^2$ art painting using BSC pixels with various *L* (2.5, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200 μm). Five CVPs of (1.5, 20, 0.0, 1000), (1.5, 20, 0.0, 3000), (1.5, 20, 0.0, 10000), (1.0, 20, 0.0, 3000), and (2.0, 20, 0.0, 3000) were applied to each group, respectively. (c) The calculated time efficiency from (b).

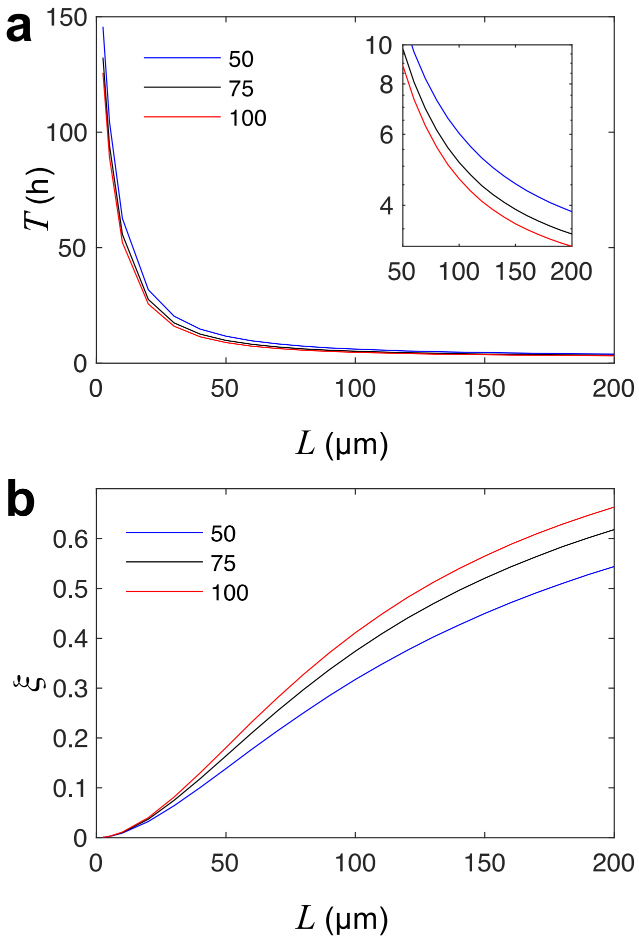


**Figure S20**. (a) The calculated time cost of TPP printing of a 1 $cm^2$ art painting using BSC pixels with constant CVP (2.0, 20, 0.0, 3000) and various $L$ (2.5, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200 μm). Various stage velocities of 50, 75, and 100 μm $s^{-1}$ were applied respectively. (b) The calculated time efficiency from (a).

**Table S1**. Time consumption on printing BSC pixels with various side lengths using constant CVP (1.0, 50, 0.0, 3000). Only galvo times were counted.

| Side length $L$ (μm) | Number of pixels $N$ | Total galvo time $T_g$ (s) | Averaged galvo time $t_g$ (s) |
|---|---|---|---|
| 1 | 14400 | 14 | 0.0010 |
| 2 | 3600 | 9 | 0.0025 |
| 3 | 2160 | 10 | 0.0046 |
| 4 | 1600 | 12 | 0.0075 |
| 5 | 1320 | 14 | 0.0106 |
| 6 | 900 | 14 | 0.0156 |
| 7 | 700 | 14 | 0.0200 |
| 8 | 600 | 15 | 0.0250 |
| 9 | 440 | 14 | 0.0318 |
| 10 | 480 | 19 | 0.0396 |
| 20 | 90 | 13 | 0.1444 |
| 30 | 49 | 16 | 0.3265 |
| 40 | 30 | 16 | 0.5333 |
| 50 | 20 | 18 | 0.9000 |
| 60 | 12 | 15 | 1.2500 |
| 70 | 12 | 20 | 1.6667 |
| 80 | 8 | 18 | 2.2500 |
| 90 | 6 | 16 | 2.6667 |
| 100 | 6 | 21 | 3.5000 |
| 110 | 6 | 24 | 4.0000 |
| 120 | 3 | 14 | 4.6667 |
| 130 | 3 | 18 | 6.0000 |
| 140 | 3 | 19 | 6.3333 |

**Table S2**. Time cost comparison of the art paintings and Zyla's work[1] (The gap between pixels was assumed as 2 μm according to the SEM images).

| | Art painting in Figure 6c | Art painting in Figure S19c | | Zyla's work |
|---|---|---|---|---|
| Print area ($mm^2$) | 1.3 × 1.3 | 8 × 8 | | 2 |
| Pixel size ($\mu m^2$) | 25 × 25 | 140 × 140 | | 11 × 4 |
| Gap between pixels $l$ (μm) | 1 | 20 | | 2 |
| Time cost per pixel $t$ (s) | 1.841 | 8.927 | | 1.685 |
| Galvo time $t_g$ (s) | 0.208 | 4.356 | 6.533 | 0.0157 |
| Line distance $a$ (μm) | 1.0 | 1.5 | 1.0 | 1.0 |
| Scan speed $v$ (μm $s^{-1}$) | 3000 | 3000 | 3000 | 1400 |
| Number of pixels $N$ | 1445 | 1022 | 423 | $2.564 \times 10^4$ |
| Total galvo time $\Sigma\ t_g$ ($s$) | 301.0 | 7215.0 | | 402.6 |
| Idle time $t_i$ (s) | 1.633 | 3.934 | | 1.669 |
| Stage time $t_{st}$ (s) | 0.446 | 2.746 | | - |
| $t_{if} + t_{se}$ (s) | 1.187 | 1.187 | | - |

| | | | |
|---|---|---|---|
| Total idle time $\Sigma\ t_i$ (s) | 2360.0 | 5685.0 | 42797.4 |
| Total time cost $T$(s) | 2661 (43 min 31 s) | 12900 (3 h 35 min) | 43200 (12 h) |
| Time efficiency $\xi$(%) | 11.31 | 55.93 | 0.93 |
| Estimated $T$(h) for 1 $cm^2$ | 43.7 | 5.6 | 600 |
| Estimated speed ($cm^2$/h) | 0.0228 | 0.1786 | 0.0017 |

**Movie S1**. Time cost for the fabrication of a single pixel with L = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 μm.

**Movie S2**. Time cost for the fabrication of a single pixel with L = 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 μm.

## References

(1) Zyla, G.; Kovalev, A.; Gurevich, E. L.; Esen, C.; Liu, Y.; Lu, Y.; Gorb, S.; Ostendorf, A. Structural Colors with Angle-Insensitive Optical Properties Generated by Morpho-Inspired 2PP Structures. *Appl. Phys. A* **2020**, *126* (9), 740.