



Cite this: DOI: 10.1039/c9tc04394b

Coffee ring elimination and crystalline control of electrohydrodynamically printed high-viscosity perovskites†

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Lead halide perovskites show enormous potential for display because of their tunable emission, high color purity, strong photoluminescence and electroluminescence. However, it is a huge challenge to achieve high resolution patterning with perfect crystalline morphologies of perovskite crystals. In this work, we combine a high-viscosity perovskite precursor with polyvinylpyrrolidone (PVP) and powerful electrohydrodynamic (EHD) printing to fabricate *in situ* crystallized high-resolution microarrays with perfect morphologies. Adding PVP contributes to reducing capillary flow to eliminate coffee rings and form spatial confinement during evaporation, limiting the flow of ions and the size of perovskite grains. However, it increases the solution viscosity, which makes printing rather difficult. This problem is solved by introducing EHD printing, which has superior advantages in high-viscosity ink printing and high-resolution patterning. Through collaborative optimization of the printing and crystallization process, the as-printed patterns and luminous images show satisfactory uniformity and high controllability in micron dimensions, and exhibit excellent compatibility with flexible substrates. This strategy is promising for wide-ranging types of optoelectronic devices.

Received 9th August 2019,
Accepted 25th September 2019

DOI: 10.1039/c9tc04394b

rsc.li/materials-c

Introduction

Hybrid perovskites are increasingly attractive owing to their excellent photoluminescence (PL)^{1,2} and electroluminescence (EL)^{3–8} properties, and they have achieved tremendous success in light-emitting diodes (LEDs),^{9,10} solar cells,¹¹ photodetectors,^{12,13} and other optoelectronic devices.^{14–19} Taking LEDs as an example, the external quantum efficiency (EQE) of perovskite LEDs has reached 20.7%,⁴ which is comparable to the commercial application level. Such applications provide immense incentives to realize microminiaturization of perovskite nanocrystals for increased integration and multifunctionality.

Research over the last several years has achieved significant progress on patterning of perovskites, which includes inkjet printing,^{20–24} nanolithography,^{25,26} and transfer printing.^{27–29} Among them, inkjet printing is the most promising technique due to its noncontact, mask-free, material-effective and large-

area production characteristics. However, challenges remain in the precise control of the evaporation and crystallization processes for printed discontinuous micro-droplets, which is critical to achieve highly uniform thin film patterns (eliminate coffee ring effect) and regulate CsPbBr₃ nanocrystal size and distribution. The coffee ring effect results from solute gathering at the pin line due to capillary flow of solution caused by an imbalance of evaporation rates at the edge and center. Two methods have been intensively applied to solve this problem. One is adjusting evaporation rate at the edge and center through mixed solvent or heating/cooling during printing to control the flow inside a droplet,³⁰ and the other one is increasing viscosity of the ink to reduce the solute movement rate.³¹ These methods bring difficulties in the preparation of the perovskite precursor ink and optimization of the printing parameters. In addition, *in situ* crystallization is definitely of great importance in optoelectronic applications. Different from applications in solar cells and photodetectors, which prefer morphologies with relatively large crystalline grains, fluorescent or electroluminescent devices prefer small and uniform crystallization. Many methods for promoting crystallization have been developed, such as anti-solvent, designed growth template, and high-temperature annealing methods.^{32,33} However, they are mainly focused on continuous films. How to realize discontinuous

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9tc04394b

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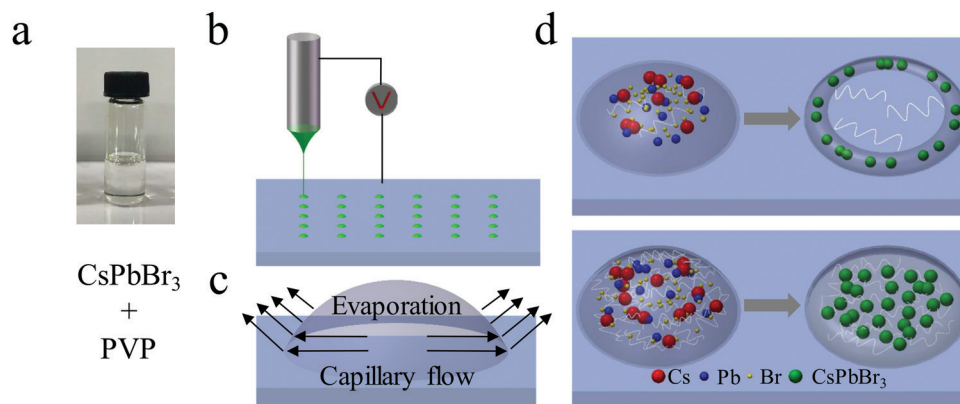


Fig. 1 (a) Image of CsPbBr₃/PVP composite ink. (b) Schematic diagram of EHD printing to form perovskite patterns. (c) Schematic diagram of the evaporation process for a printed droplet. (d) Schematic diagram of crystallization processes with or without “coffee ring” related to different PVP concentrations.

microminiaturization of high-quality perovskite nanocrystals is still challenging.

In this paper, we combine a high-viscosity perovskite precursor with polyvinylpyrrolidone (PVP) and powerful electrohydrodynamic (EHD) printing^{34–38} to successfully achieve high-resolution patterning and good crystalline morphologies of perovskite. Adding PVP into the perovskite precursor increases the solution viscosity, which can increase the moving resistance and eliminate the coffee ring effect. Meanwhile, the polymer causes spatial confinement during evaporation, which is beneficial for small and uniform crystallization. EHD printing utilizes a high electric field to introduce a tangential stress on the liquid surface, thereby deforming the meniscus into a conical shape from whose vertex a fine jet is ejected. It exhibits superior advantages of high resolution (<1 μm) and compatibility with a wide viscosity range of inks (1–10 000 cP), such as PEDOT:PPS,³⁹ silver nanoparticles⁴⁰ and many others.^{41,42} The as-printed CsPbBr₃/PVP microarrays emit bright green light with a PL peak centered at 519 nm and a narrow FWHM of 18 nm. Various complex patterns, such as the complicated logo of Huazhong University of Science and Technology, Plum blossom and elephant, could be printed on rigid or flexible substrates. The EHD-printed patterns with uniform small grains show homogeneous and bright PL on a microscale without pre-synthesis of a luminescent precursor, which is suitable and cost-effective for large-area, long-time printing and has huge potential in display and other fields.

Results and discussion

Fig. 1 depicts the *in situ* crystallization process of perovskite nanocomposites using the EHD printing technique. The precursor ink for EHD printing is composed of cesium bromide (CsBr), lead bromide (PbBr₂), PVP and the solvent dimethyl sulfoxide (DMSO), as shown in Fig. 1a. In order to tune the viscosity of the precursor ink for EHD printing, we changed the concentration of PVP. As the PVP concentration increases, the viscosity of the precursor ink enhances along with the

Table 1 Viscosity and contact angle of perovskite inks with different PVP concentrations

Concentration of PVP (mg mL ⁻¹)	100	200	300	400	500
Viscosity (cP)	10.39	41.47	70.57	233.67	610.33
Contact angle	10.88°	16.20°	20.24°	26.03°	30.25°

contact angle (Table 1 and Fig. S1 and S2, ESI†). The five solutions with PVP concentrations of 100, 200, 300, 400, and 500 mg mL⁻¹ have viscosities of 10.39, 41.47, 70.57, 233.67, and 610.33 cP, and contact angles of 10.88°, 16.20°, 20.24°, 26.03°, and 30.25°. The above viscosity is far out of the printable range (5–20 cP) of traditional inkjet printing. To solve this problem, we introduce EHD printing to print higher viscosity inks and simultaneously achieve higher resolution. In Fig. 1b, EHD printing applies a square wave (Fig. S3, ESI†) to the nozzle plated gold to form an electric field between the nozzle and the substrate, polarizing the solution at the tip of the nozzle and using the electric field force to pull the ink out to form dot arrays. The droplet reaching the substrate forms a spherical cap with relatively uniformly distributed perovskite precursor and long-chain PVP molecules. However, this uniformity is normally broken with the evaporation of the solvent, which will lead to some peculiar effects. Fig. 1c and d show the process of droplet evaporation and crystallization for the perovskite. The volatilization velocity of the droplet is greater at the edge than in the middle, which results in a concentration gradient, and further forms a capillary flow from low concentration to high concentration, *i.e.* from the middle of the droplet to the edge of the droplet (Fig. 1c). This capillary flow leads to solute accumulation at the edge, which means that Cs, Pb, and Br ions will combine to flow along the capillary flow from middle to edge. When the concentration of the perovskite precursor reaches its critical value for nucleation, CsPbBr₃ nanocrystals with coffee rings are formed (upper image of Fig. 1d). If this capillary flow is limited, Cs, Pb and Br ions will distribute uniformly during evaporation, thus a uniform film without a coffee ring will be formed, as shown in the lower image of Fig. 1d.

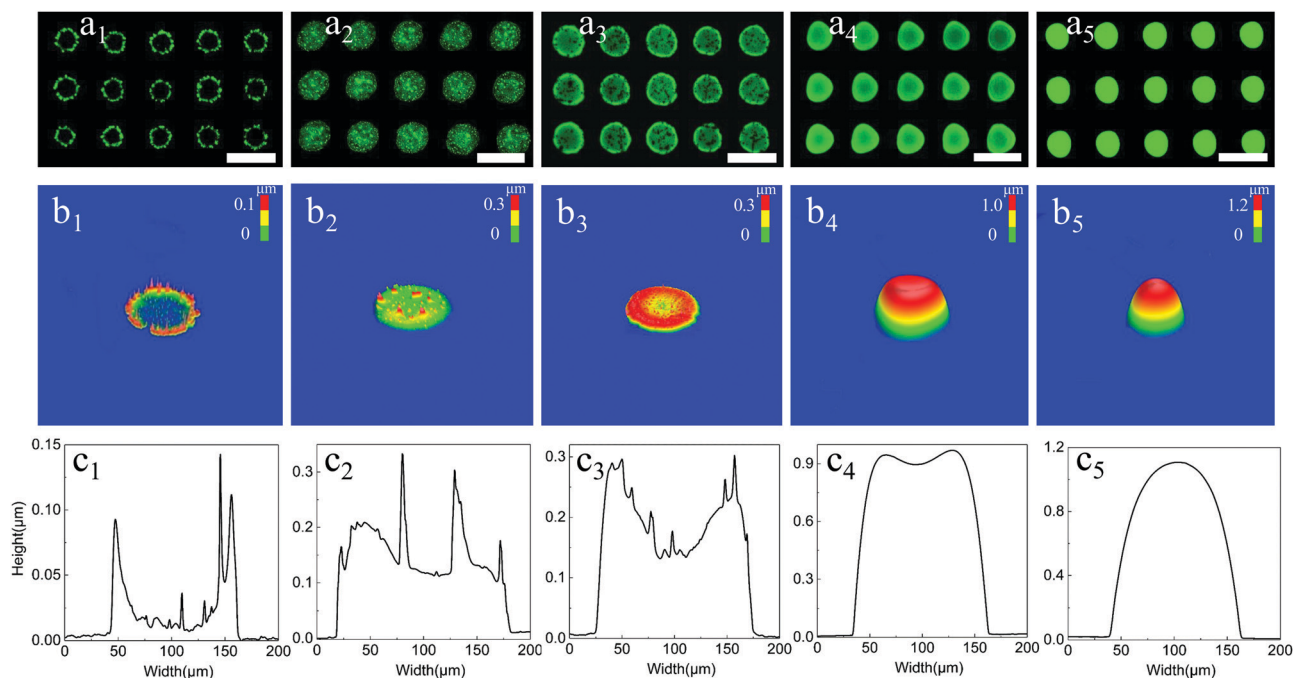


Fig. 2 (a1–a5) Fluorescence microphotographs of dot arrays printed with different PVP concentrations. The scale bar is 200 μm . (b1–b5) Three-dimensional white light interferometer images and (c1–c5) film thickness profiles of each single dot printed with different PVP concentrations.

To eliminate the coffee ring caused by uneven evaporation and capillary flow, while considering the nucleation and growth of crystals, the effects of PVP concentrations are carefully investigated. Fig. 2a shows fluorescence pictures of dot arrays evaporated at room temperature with different PVP concentrations of 100, 200, 300, 400, and 500 mg mL^{-1} , and the corresponding white light interferometer pictures and film thickness profiles are shown in Fig. 2b and c. The results indicate that the coffee ring is weakened and photoluminescence is enhanced with the increase of PVP concentration. As mentioned above, the perovskite precursor and PVP uniformly distributed in the droplet at first. Along with the evaporation of solvent, PVP spontaneously forms a closed interval, which restricts the flow of ions including Cs, Pb, and Br ions and the solutes are assembled in space. Adding PVP corresponds to a larger viscosity in the droplet, which means that the capillary flow is much more limited due to a larger moving resistance, thus well-distributed ions can be formed. Meanwhile, more PVP represents more smaller confined spatial isolation, which is beneficial for forming small-sized crystal grains during the evaporation process (Fig. S4, ESI†). When the PVP concentration reaches 500 mg mL^{-1} , the coffee ring is totally inhibited and small crystal grains are formed, which demonstrate improved PL intensity.

The effects of substrate temperature on the evaporation and crystallization of EHD printed dot arrays are also investigated, as shown in Fig. S5 (ESI†). According to the theory of capillary flow, heating during printing definitely aggravates the coffee ring. As for the perovskite solution with a low PVP concentration, when printing on a room-temperature substrate, the slow evaporation and crystallization rate favors the growth of large crystal grains. When printing on a heated substrate, *e.g.* 40 $^{\circ}\text{C}$, although small crystal grains are formed because of fast crystallization, the

coffee ring is aggravated due to severe evaporation and fast capillary flow.

To study the influence of post-annealing temperature on perovskite microarrays, we designed three groups of experiments with annealing temperatures of 80, 100 and 120 $^{\circ}\text{C}$. Fig. 3a shows the XRD patterns of the $\text{CsPbBr}_3/\text{PVP}$ microarrays. The main diffraction peaks at 15.2 $^{\circ}$ (100), 21.6 $^{\circ}$ (110), and 30.5 $^{\circ}$ (200) in the pattern are identified as the characteristic peaks of CsPbBr_3 nanocrystals, indicating that the CsPbBr_3 microarrays are in a cubic phase and in contrast to the standard phase of CsPbBr_3 . After annealing at 100 and 120 $^{\circ}\text{C}$, diffraction peaks of CsPbBr_3 are more obvious, illustrating better crystallinity of perovskite than at 80 $^{\circ}\text{C}$. Fig. 3b shows that the relative photoluminescence intensity of the microarrays reaches its maximum value at 100 $^{\circ}\text{C}$. The absorption and PL spectra of the brightest $\text{CsPbBr}_3/\text{PVP}$ microarrays are shown in Fig. 3c. The as-synthesized microarrays exhibit a weak absorption peak at 509 nm and a PL peak centered at 519 nm. A Stokes shift from 509 to 519 nm exists between the emission and the band-edge absorption. Besides, the narrow FWHM of 18 nm suggests that the as-synthesized CsPbBr_3 microarrays have a centralized crystal size distribution and uniform crystallinity. The time resolved PL decays of CsPbBr_3 microarrays with or without PVP, as well as the corresponding exponential fitting curves are shown in Fig. 3d. The average PL lifetime (PL intensity decreases to 1/e of the initial intensity) of CsPbBr_3 microarrays with PVP is 123.45 ns longer than 26.37 ns of CsPbBr_3 microarrays without PVP. The addition of PVP increases the probability of radiative recombination and PL intensity.

Fig. 4 demonstrates the promising advantages of our EHD printing for large-area, high-resolution patterning and flexible application. Fig. 4a–c show the fluorescence images of microscale

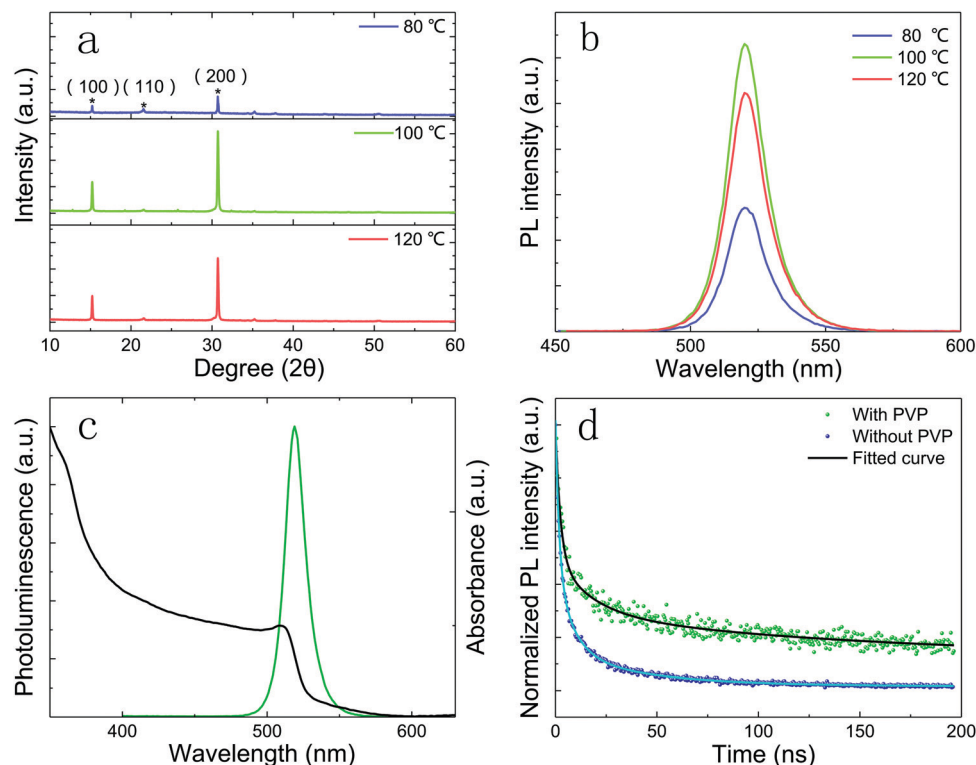


Fig. 3 Optical properties of CsPbBr₃/PVP nanocomposite microarrays. (a) XRD patterns and (b) PL spectra of CsPbBr₃/PVP microarrays at different annealing temperatures. (c) Absorption and PL spectra of the brightest CsPbBr₃/PVP microarrays. (d) Time-resolved PL decays of CsPbBr₃ microarrays with or without PVP.

dot arrays and line arrays, which emit highly homogeneous and bright green light under UV light stimulation. By using smaller-size nozzles while optimizing the driving voltage, dot arrays with diameters of $\sim 5 \mu\text{m}$ have been successfully achieved, which can satisfy most applications in lighting or displaying. In Fig. 4d, the fluorescence image of the school badge of Huazhong University of Science and Technology (HUST) is composed of green emitting dot patterns and shows bright PL on the macroscale. The enlarged fluorescence images and 3D images of the white light interferometer picture demonstrate the excellent repeatability and uniformity of every single dot. Fig. 4e–h confirm that this technology is capable of printing more complex patterns, such as flowers and elephants in combination with the substrate movement control. Furthermore, this strategy also shows excellent compatibility with flexible substrates with a thickness of $50 \mu\text{m}$, as shown in Fig. 4i and j, where various complex patterns can be printed on a flexible polyimide substrate.

Conclusions

In summary, we combine a high-viscosity perovskite precursor with PVP and powerful EHD printing to achieve high-resolution patterning and good crystalline morphologies of perovskite successfully. Long-chain PVP is added into the perovskite solution to increase the viscosity and the contact angle of the precursors, thus reducing the capillary flow and eliminating the coffee ring. High concentration PVP forms multiple small spaces

during evaporation, limiting the flow of ions and preventing the appearance of large grains. EHD printing offers powerful capabilities in patterning perovskite solution with a wide range of viscosity, and various homogeneous patterns, such as dots, lines, and complex images, that have been achieved. The printed images show homogeneous and bright PL on a microscale without any substrate heating and vacuum drying, and the dot size can be tuned as small as $5 \mu\text{m}$. This strategy also shows excellent compatibility with flexible substrates, and is suitable for large-area, long-time printing, demonstrating its huge potential in various optoelectronic applications, such as light emitting diodes, transistors and photodetectors.

Experimental section

Perovskite precursor preparation

Lead bromide (PbBr₂, 99.9%), cesium chloride (CsBr, 99.9%), polyvinylpyrrolidone (PVP, average molecular weight $\sim 40\,000 \text{ g mol}^{-1}$), and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. 2-Phenylethanamine bromide (PEABr, 99%) was purchased from Xi'an polymer light technology corp. 18-Crown-6 was purchased from Aladdin Reagent. All reagents were used without further purification. The perovskite inks were obtained by mixing 0.2 mmol of CsBr, 0.2 mmol of PbBr₂, 0.16 mmol of PEABr and 3.5 mg of 18-crown-6 in 1 mL of DMSO at 80°C for 2 h with constant stirring. Different amounts of PVP were added into the mixed perovskite precursor at 60°C stirring for

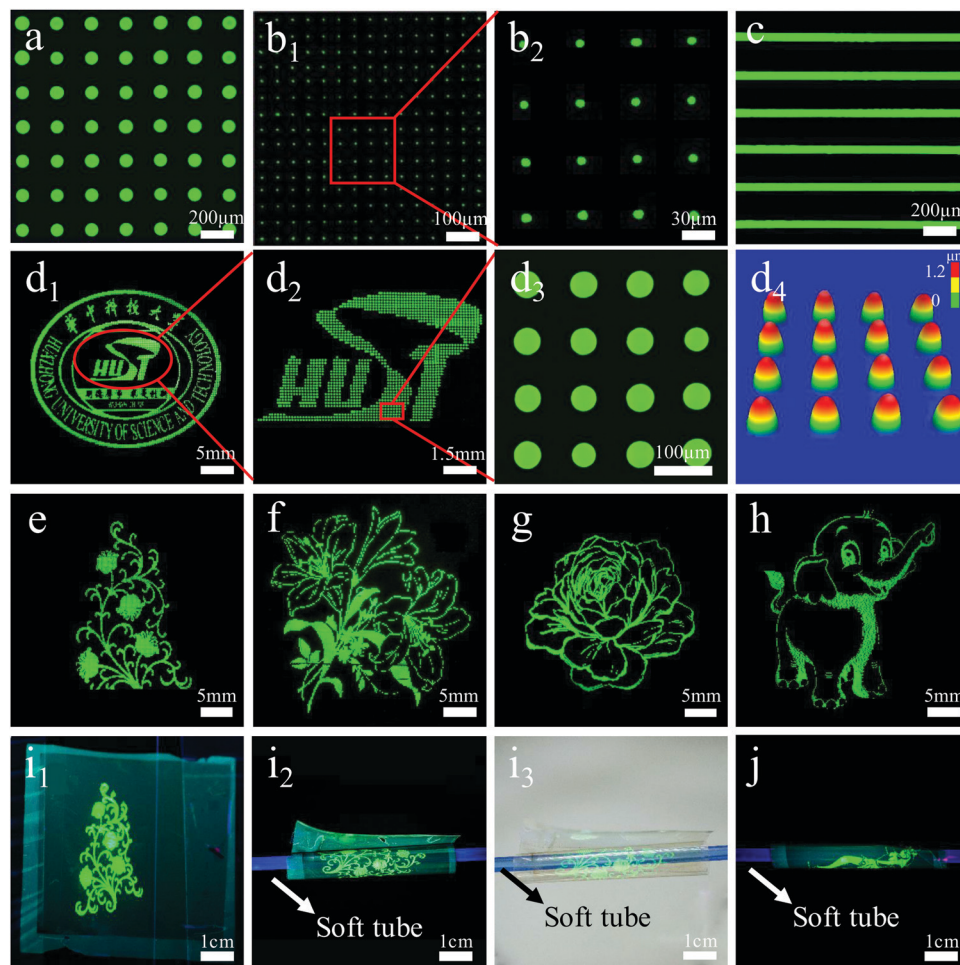


Fig. 4 (a) Microscale dot arrays. (b₁ and b₂) A high-resolution dot matrix with a CsPbBr₃/PVP dot diameter of ~ 5 μm . (c) Microscale line arrays. (d₁–d₄) The school badge of Huazhong University of Science and Technology, local enlarged fluorescence images and 3D images of white light interferometer pictures of dot matrices. (e) Flower type pattern. (f) Lily pattern. (g) Rose pattern. (h) Elephant pattern. (i₁–i₃) Flower type patterns on flexible substrates in a dark room or a bright room. (j) Sun Wukong pattern on a flexible substrate.

2 h to get perovskite inks with different concentrations of PVP. All the perovskite inks were filtered by 0.45 μm hydrophobic poly(tetrafluoroethylene) syringe filters before using. And all the processes were carried out in a clean room.

Electrohydrodynamic printing process

ITO-coated glass substrates were cleaned by ultrasonication successively in acetone, isopropyl alcohol, and deionized water in sequence. The substrates were dried by using flowing nitrogen gas. The printing process was accomplished by using a high resolution electrohydrodynamic inkjet printer (HEIJ-P professional type, Wuhan Huawei Intelligent Technology Co., Ltd) equipped with a waveform generator (33500B Series, Keysight Technologies, Japan), a high-voltage amplifier (MODEL 609E-6, Trek Inc., USA) and a motorized stage with an accuracy of ± 3 μm . The perovskite ink was injected to a glass capillary, whose diameter at the tip of 5 or 40 μm was sputter-coated with gold/chromium. Gold plating increases the conductivity of the glass capillary, and chrome plating increases the adhesion of gold. By applying a high voltage of about 1200–1300 V on the metal-coated glass capillary and a

height of about 50–100 μm between the ITO substrate and the nozzle tip, dot arrays can be deposited. The above process was carried out at room temperature under ambient conditions. After printing, the ITO substrate with a perovskite pattern was annealed at 100 $^{\circ}\text{C}$ in a glove box for 10 min to complete crystallization. The flexible perovskite patterns were obtained by first spin coating a layer of polyimide (PI) and sputtering a layer of ITO on a glass substrate, and then printing dot arrays on the PI substrate through EHD printing, and finally stripping the PI from ITO by using a laser lift-off technique.

Characterization

The properties of perovskite inks, including contact angle and viscosity, were obtained from an automatic contact angle measuring instrument (Corona, SL200KB) and a discovery hybrid rheometer (TA Instruments, HR-1) at room temperature. The 3D images of dot microarrays were characterized by white light interferometry (ZYGO, NewView 7100). The PL images of the printed microarrays were characterized by using a fluorescence microscope (Nikon eclipse Ts2R). X-ray diffraction (XRD) analysis

was performed on a XRD-6000 X-ray diffractometer (Shimadzu) with Cu Ka radiation ($\lambda = 1.5406 \text{ \AA}$). UV-vis spectrophotometry (SHIMADZU, SolidSpec-3700 using an integrating sphere) was used to study the optical absorption of the perovskite film. An edinburgh instruments FLS 980 spectrometer, xenon lamp, TCSPC module (diode laser excitation at $\lambda = 365 \text{ nm}$), red-sensitive photomultiplier (R928) and integrating sphere were used to record the steady-state and time-resolved PL (TRPL) spectra of the microarrays. The surface of the microarrays was measured by field emission scanning electron microscopy (FE-SEM, FEI NOVA NanoSEM 450). The laser lift-off equipment was a homemade facility of the State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was financially supported by the National Key Research and Development Program of China (2016YFB0401105) and the National Natural Science Foundation of China (51605180 and 51635007). The authors would also like to thank the Flexible Electronics Manufacturing Laboratory in Comprehensive Experiment Center for advanced manufacturing and equipment technology.

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