Ion exchange, self-assembly, and light emission

A dance of ions and light

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Radiant
Ion Exchange Lithography on Lead Carbonate, 2020
Lukas Helmbrecht

CHAPTER 4

Ion Exchange Lithography: Localized Ion Exchange Reactions for Spatial Patterning of Perovskite Semiconductors and Insulators

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Patterning materials with different properties in a single film is a fundamental challenge and essential for the development of next-generation (opto)electronic functional components. This work introduces the concept of ion exchange lithography and demonstrates spatially controlled patterning of electrically insulating films and semiconductors with tunable optoelectronic properties. In ion exchange lithography, a reactive nanoparticle "canvas" is locally converted by printing ion exchange "inks". To demonstrate the proof of principle, a canvas of insulating nanoporous lead carbonate is spatioselectively converted into semiconducting lead halide perovskites by contact printing an ion exchange precursor ink of methylammonium and formamidinium halides. By selecting the composition of the ink, the photoluminescence wavelength of the perovskite semiconductors is tunable over the entire visible spectrum. A broad palette of conversion inks can be applied on the reactive film by printing with customizable stamp designs, spray-painting with stencils, and painting with a brush to inscribe well-defined patterns with tunable optoelectronic properties in the same canvas. Moreover, the optoelectronic properties of the converted canvas are exploited to fabricate a green light-emitting diode (LED), demonstrating the functionality potential of ion exchange lithography.

4.1 Introduction

Spatial arrangement of materials with contrasting properties is fundamentally interesting and essential for integrated (opto)electronic devices.[3,77] Nanoparticles are versatile building blocks for achieving such arrangement by both bottom-up and top-down assembly.[8,9,11,14,33,34,38,39,48,77–87,163] Spatial patterning of nanoparticles has been achieved by methods such as patchy particles, oriented attachment, hierarchical self-assembly, topological templates, and optical and e-beam lithography.[8,9,11,14,33,34,38,39,77–82,163,164] Moreover, the entire ensemble of nanoparticles can be converted into a desirable chemical composition using ion exchange reactions, while preserving the pattern of the ensemble.[34,48,83–87] Also, selected areas of the ensemble can first be encapsulated with a passivating coating, after which only the uncoated nanoparticles undergo conversion during ion exchange.[95] Hence, organization of different composition is possible in many ways, but oftentimes requires multiple steps to achieve control over patterning and chemical composition, making the overall process difficult and expensive.[77,82]

Locally applying the reagents offers an alternative approach for spatial arrangement of materials with desirable properties. For thousands of years, printing of inks on canvases has spurred human development. Recently, methods such as microcontact printing have been used extensively to locally functionalize substrates and infuse reactants in gels.[165–168] Inspired by these works, we here introduce the concept of ion exchange lithography (IEL). We show that spatial patterning of materials can simply be achieved by printing ion exchange "inks" on a reactive nanoparticle "canvas". Importantly, to act as a versatile canvas, the nanoparticle film should enable ion exchange to many different chemical compositions. The ink, on the other hand, should react the contacted area of the canvas to one specific composition only, while other reaction products ideally leave the canvas automatically.

To demonstrate the proof-of-principle of IEL, we explore the spatially controlled conversion of an electrically insulating canvas into semiconducting lead halide perovskites. The extraordinary properties of perovskites, in combination with their simple synthesis, is revolutionizing the field of optoelectronics.[102–104] Spatially organizing perovskites alongside materials with fundamentally different properties is essential for integrated devices such as displays, detectors, and scintillators.[107–112] Spatial positioning of perovskites has been achieved using, for instance, photolithography, laser writing, templates, and inkjet printing.[114–119,121] Post synthesis modification of perovskites has enabled local modification of the light emission color.[96,113] Nevertheless, such approaches are often laborious and slow, and require specialized equipment, thus making them difficult to scale up. This highlights the need for new strategies to directly achieve spatial organization of desirable compositions in a simple and scalable manner.

Here we integrate semiconducting perovskites in an electrically insulating film by printing, painting, and spraying reactive inks on an ion-exchange reactive canvas. The versatility of this IEL approach allows for scalability and arbitrary, user-defined patterns. The photoluminescence wavelength of the perovskite semiconductors is tunable over the entire visible spectrum by selecting the composition of the ink. Moreover, we show that the IEL approach can be integrated into the fabrication of (opto)electronic devices such as light-emitting diodes (LED).

4.2 Results and Discussion

Our approach is illustrated in Figure 4.1. In short, nanoscopic lead carbonate ($PbCO_3$) crystals are deposited in a thin film. This electronically insulating lead carbonate ($PbCO_3$) film acts as reactive canvas, while a solution of methylammonium halides (CH_3NH_3X or MAX; X = Cl, Br, or I) is the reactive ink. Contact printing of the ink on the canvas results in the local conversion of $PbCO_3$ into semiconducting methylammonium lead halide perovskites ($CH_3NH_3PbX_3$ or $MAPbX_3$; X = Cl, Br, or I) following the previously developed reaction:[48]

$$\begin{gathered} PbCO_3(s) + 3CH_3NH_3X(l) \rightleftharpoons \\ H_2O(l) + CO_2(g) + 2CH_3NH_2(g) + CH_3NH_3PbX_3(s) \end{gathered} \tag{4.1}$$

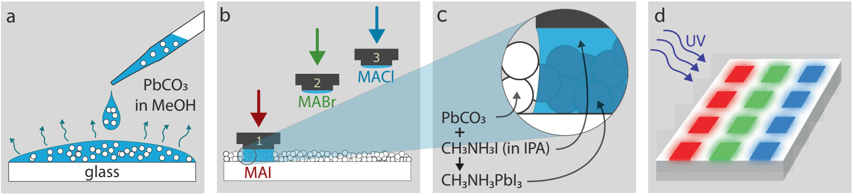

FIGURE 4.1: Schematic illustration showing the fabrication of a spatially patterned perovskite film. a) Drop casting $PbCO_3$ particles dispersed in methanol onto a glass substrate results in a $PbCO_3$ thin film that acts as the reactive canvas. b) Stamping MAX in IPA on the canvas results in, c) spatially-controlled conversion of the $PbCO_3$ into a $MAPbX_3$ perovskite. d) Upon UV irradiation, the converted areas emit light with a color that is controlled by adjusting the halide moiety of the perovskite.

To demonstrate the proof-of-principle, we fabricate nanoporous films by drop casting nanoscopic $PbCO_3$ crystals onto glass substrates (see Methods for details). High-resolution Scanning Electron Microscopy (SEM) shows that the particles have typical sizes between 40 and 300 nm, and are densely packed into uniform films while still exhibiting nanoscale porosity (Figure 4.2a). We find that the film thickness can be tuned between ca. 0.25 and 5.0 µm by controlling the drop casting conditions (Figure 4.2 and Methods).

We perform the ion exchange contact printing by bringing the $PbCO_3$ film in contact with a solution of MAX in anhydrous isopropyl alcohol (IPA). The conversion ink is applied using customized silicone stamps (see Methods). Silicone is easily moldable and chemically inert. In addition, the hardness of the silicone can be tuned to achieve uniform contact while keeping the canvas intact during removal of the stamp (see Methods).[165,168] The local conversion is demonstrated by applying MABr-IPA on the $PbCO_3$ canvas using a stamp patterned with rectangular studs. Within seconds the white $PbCO_3$ transforms into yellow-orange perovskite at the points of contact with the stamp, thereby meticulously replicating the pattern of the stamp with high fidelity (See Methods for comparison of a stamp and stamped pattern). The optoelectronic properties of the converted pattern can directly be visualized by exciting the electronic structure with an ultra-violet (UV) light source (Figure 4.2b). We observe bright green photoluminescence (PL) from the converted rectangles, whereas the lead carbonate in the pristine part of the film did not convert to the perovskite and therefore did not emit any light. Photoluminescence spectroscopy showed that the emission wavelength of the converted pattern peaked at 530 nm, which is consistent with previous PL measurements of $MAPbBr_3$.[48]

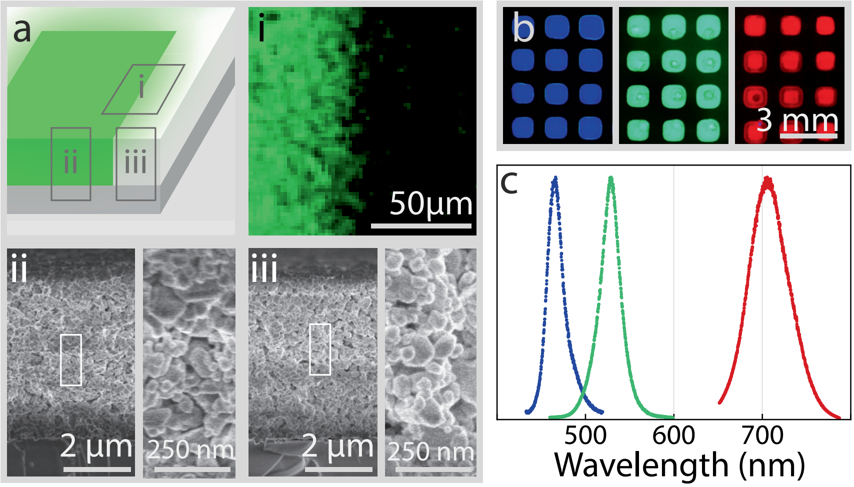

FIGURE 4.2: Characterization of contact printed perovskite pixels. a) Schematic overview of a printed pixel: i) EDS elemental mapping of Br atoms, ii) cross-section of a converted film with close-up (SEM), iii) cross section of a pristine film with close-up (SEM). b) Fluorescence photographs of contact printed perovskite pixels of different emission colors by tuning the halide moiety: left to right: MACl-MABr (6:4), MABr, MABr-MAI (2:8). c) Corresponding normalized photoluminescence spectra of the perovskites shown in b).

We expect that the nanoporous structure facilitates percolating by capillary forces to achieve conversion throughout the interior of the canvas. Indeed, energy-dispersive X-ray spectroscopy (EDS) on a cross-sectioned sample reveals the presence of bromide throughout the depth of the canvas (see Methods, Figure M4.3). Combined with fluorescence photographs of the backside of the opaque canvas, this indicates conversion from the top to the bottom (see Methods, Figure M4.2). Still, in the lateral direction, a well-defined boundary between the converted and unconverted area is achieved, according to EDS (Figure 4.2a). Although the grains undergo conversion to perovskite, the nanoscopic morphology is conserved, as observed via high-resolution electron microscopy (Figure 4.2a). Furthermore, EDS analysis suggests that mostly the outside of these grains is converted, as ca 3.5 at% of the film constitutes of bromide, while the surplus $PbCO_3$ in the grains may support the morphology retention. We expect that the degree of conversion can be further controlled through the balance between $PbCO_3$ and conversion ink, as well as the size of the particles themselves.

Reaction scheme 4.2 suggests that perovskites with different halide moieties–and therefore different emission colors–can be synthesized in the $PbCO_3$ film by selecting the corresponding methylammonium halide precursor in the ink. Indeed, mixing MAI into the MABr/IPA conversion ink yielded mixed-halide perovskite patterns with red PL, while MACl addition resulted in blue PL (Figure 4.2b). The emission wavelength can be tuned by the mixing ratios of different methylammonium halides in the conversion ink: e.g., 6:4 molar ratio MACl:MABr/IPA resulting in bright emission around 465 nm (Figure 4.2c), whereas 8:2 molar ratio MAI:MABr yields deep red emission around 705 nm (Figure 4.2c). Hence, the color of the light-emitting patterns can be tuned over the whole visible spectrum.

IEL can be extended to other classes of perovskites. Formamidinium halide perovskites ($CH(NH_2)_2PbX_3$ or $FAPbX_3$; X = Cl, Br, or I) are of interest because of their greater chemical stability and longer carrier diffusion length while exhibiting comparable optical performance compared to methylammonium perovskites.[169,170] Conversion of $PbCO_3$ to $FAPbX_3$ is achieved using formamidinium halides ($CH(NH_2)_2X$ or FAX; X = Cl, Br, or I) instead of methylammonium halides in the precursor ink. Akin to MAX (reaction scheme 4.2), FAX can partly dissociate to form acid and thereby drive the exchange of carbonate with the halide group. Moreover, the chemical similarities between MAX and FAX as well as the structural similarities between the crystal lattices of $MAPbX_3$ and $FAPbX_3$ suggest an equivalent reaction pathway. The resulting $FAPbX_3$ perovskite patterns show bright luminescence with tunable PL emission throughout the visible spectrum by selecting the halide moiety between chloride, bromide, and iodine (see Appendix).

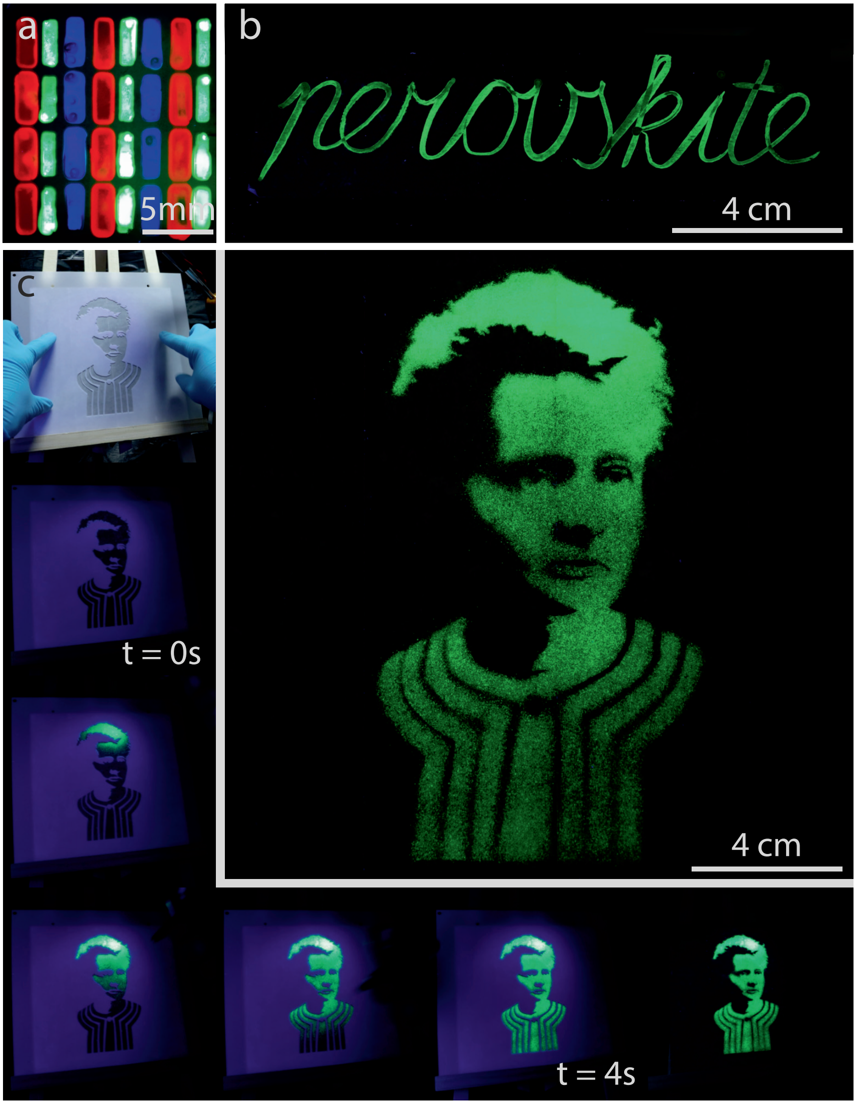

FIGURE 4.3: IEL via different printing techniques. a) Fluorescence photograph of multicolor contact printed pixels: FABr-FAI (2:8) (red), MABr (green), and MACl-MABr (6:4) (blue) separated by unconverted $PbCO_3$. b) Fluorescence photograph of a pattern drawn by applying the conversion ink with a paintbrush. c) Time-lapse of an airbrush painting of Marie Skłodowska-Curie: a 20x20 cm film of $PbCO_3$ is selectively shielded with a stencil (the polymer in the stencil fluoresces blue under UV irradiation), MABr/IPA is applied with an airbrush gun, the ion exchange reaction creates perovskite that luminesces green under UV irradiation, removal of the stencil shows the portrait.

Based on these insights, we integrate perovskites with different emission wavelengths into a single canvas. To this aim, we sequentially print the ion mixtures for different perovskites on the lead carbonate film. Accurate spatial positioning of the different stamps is achieved by a guiding framework (see Methods, Figure M4.2). To demonstrate the principle, we integrate rectangles of red, green, and blue-emitting semiconductors within the non-luminescent insulator to produce an array pattern akin to the ones commonly used in LED displays (Figure 4.3a).

The ion exchange inks could be applied using many other traditional and scalable inking techniques such as inkjet-, offset-, and roll-to-roll printing. From this extensive repertoire, we test traditional artist's paintbrushes and an airbrush gun. With the paintbrush, freeform patterns can be achieved straightforwardly (Figure 4.3b). With the airbrush, large uniform areas can be converted. Moreover, highly complex patterns can be achieved using laser-cut stencils as a shadow mask, which we exploit for creating a green luminescent portrait of Marie Skłodowska-Curie. (Figure 4.3c). An additional advantage of airbrushing is that this method is fast and contact-free while easily converting sizeable areas, hence averting the risk of damaging the film and offering compatibility for large-scale fabrication.

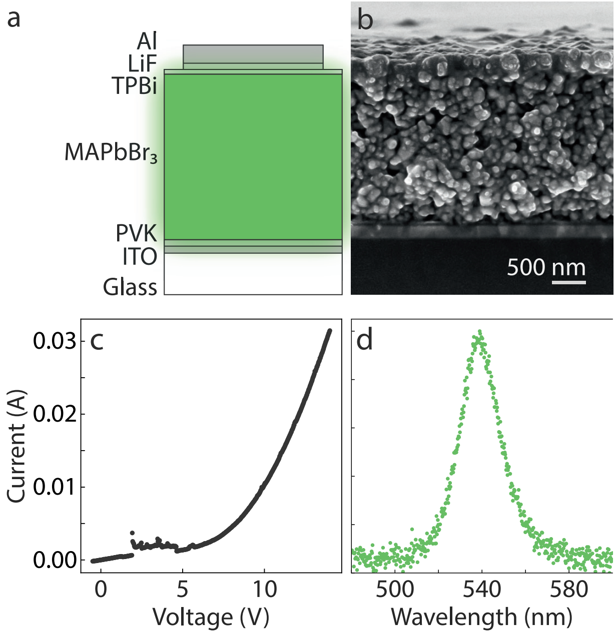

FIGURE 4.4: LED based on an IEL. a) Schematic of the layers used in this LED. b) Cross section of a device imaged by SEM. c) IV measurement. d) Normalized EL showing green light emission of the LED at 10 V.

IEL offers exciting opportunities for the direct integration of materials with different electronic properties in functional devices. We demonstrate the principle for a LED with $FAPbBr_3$ as the active layer. The device is constructed of stacked layers with, in the center, the perovskite created by ion exchange (see Figure 4.4a, b and Methods 4.4.4). We characterize the device by performing electroluminescence (EL) spectroscopy and measuring the current-voltage (IV) curves. As expected for $FAPbBr_3$ LEDs, the IV curves display typical diode characteristics (Figure 4.4c). With applied voltage, the device operates as an LED and emits green EL around 540 nm as previously reported,[171,172] demonstrating the potential of IEL for functional (opto)electronic devices (Figure 4.4d).

4.3 Conclusion

In conclusion, we here demonstrate spatially-controlled ion exchange reactions of lead carbonate films into lead halide perovskites. We show that this ion exchange-lithography method offers a simple, scalable, versatile, and highly customizable method for integrating desirable complementary electronic and optoelectronic properties in arbitrary patterns that can be integrated into functional devices. Effectively, the conversion liquid and film can be regarded as reactive ink and canvas for integrating unusual and attractive properties with high spatial control.

Semiconductors and lead carbonates have a long history in painting and other arts. Basic lead carbonate is one of the oldest synthetic pigments known, while semiconducting salts such cadmium sulfide and lead chromate enabled bright colors and were widely adopted by painters such as Monet and Van Gogh.[173–176] Traditionally, artists apply the semiconductors as pigment on the canvas. In contrast, our work enables conversion of the canvas into a semiconductor by painting a reactive ink.

Already, many ion exchange reactions have been developed in liquids.[48,83–86] We therefore envisage that the palette of conversion inks for our IEL methodology can straightforwardly be extended to a wide range of chemical compositions with desirable and unusual properties. Moreover, state-of-the-art technologies such as roll-to-roll and inkjet printing can be exploited, since the resolution of the converted patterns is to a large extend defined by the precision with which the conversion ink is applied. In addition, we foresee that nanocomposites could serve as attractive conversion canvases due to their outstanding mechanical properties and chemical reactivity.[48,177–179] Consequently, IEL may offer an attractive route for the synthesis of functional integrated devices such as displays and detectors that require complicated spatial patterning of complementary properties in a single film. Therefore, exciting opportunities will arise from expanding the microelectronic paint box, adding conversion inks for the synthesis of other semiconductors, transport layers, and conductors, which ultimately enables fully printed devices with ion exchange lithography.

4.4 Methods

4.4.1 Lead Carbonate Canvas Fabrication

Lead carbonate powder (2.0 g, Alfa Aesar, lead(II)carbonate, ACS, 40119) was dispersed in 10 ml isopropyl alcohol with glass beads in a 20 ml vial, and ground for ten consecutive days in an ultrasonic bath (VWR Ultrasonic Cleaner USC-THD). Subsequently, the nanocrystalline lead carbonate powder was isolated from the slurry by filtration. To prepare the canvas, the nanocrystals were dispersed in methanol (25 mg $PbCO_3$/ml MeOH) and sonicated for 180 minutes at room temperature. Microscope slides were cut to 15x15 or 17x17 mm squares, cleaned with isopropyl alcohol, and plasma cleaned for 10 minutes. Typically, 150–200 µl of the $PbCO_3$/MEOH was drop casted onto each substrate. To obtain the canvas, the solvent was left to evaporate at 45 °C in an oven. Thinner films were achieved by diluting the dispersion (Figure M4.1). The lead carbonate canvas used for the airbrushed portrait and the “perovskite” lettering was obtained by covering a 20x20 cm ceramic tile with double-sided tape and brushing lead carbonate onto it (see also M4.2g).

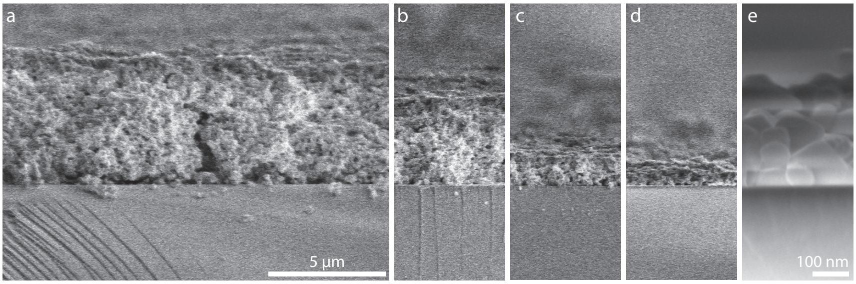

FIGURE M4.1: Lead carbonate nanoparticle films of decreasing thickness. a) 5 µm film created with stock solution. b–e) Dilution of the dispersion allows for thinner films. Note the higher magnification in e).

4.4.2 Contact Printing Perovskites

Stamps were prepared from commercially available silicone (Zhermack elite double, 32 shore). The silicone is available in a variety of degrees of hardness. We find that softer stamps damage the film, whereas harder stamps fail to make uniform contact. The stamps were fabricated by casting the liquid silicone into 3D printed molds. We designed patterns with 1x1 mm studs and 1 mm spacing, as well as a pattern of 1.5x3 mm studs. The later pattern was split into three parts on three stamps for sequential application (Figure M4.2). The conversion ink was prepared by dissolving 0.16 mmol methylammonium or formamidinium halide per ml isopropyl alcohol under inert environment. The crucial parameters for successful stamping are the amount of ink that is transferred and the applied pressure. To control the amount of liquid, 25 µl conversion ink is placed in a petri dish. A 20x20 mm piece of foam board is pressed onto that drop. The stamp is inked by gently pressing it against the foam board. To contact print the $PbCO_3$, the stamp is gently pressed on the canvas, assuring sufficient contact pressure to transfer the ink without damaging the canvas.

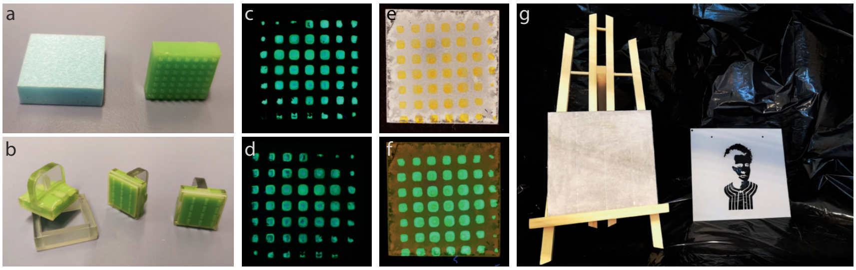

FIGURE M4.2: Printing and painting of perovskites. a) Foam board for ink transfer and silicone stamp. b) Silicone stamps with guiding frame to integrate different compositions, c) and d) perovskite pattern on glass, imaged from the front and backside, respectively, showing conversion throughout the film. f, g) Perovskite pattern in daylight and with additional UV light, respectively. c) Setup for airbrush painting with a stencil.

4.4.3 Characterization of Perovskite Samples

The fluorescent nature of the perovskites is a convenient first indicator of successful conversions. Illuminated with a UV LED (365 nm), the converted parts light up. The photographs in Figures 4.2 and 4.3 were taken with a Canon 800D camera equipped with a Sigma 17-70 mm macro lens and a UV filter. Scanning electron microscopy micrographs were captured with an FEI Verios 460. The EDS (energy dispersive X-Ray spectroscopy) map of bromide distribution was recorded with an additional Oxford X-Max^n energy dispersive X-ray spectrometer (Figure 4.2 and M4.3). Photoluminescence was studied using a Witec alpha 300 in combination with a Thorlabs S1FC405 405 nm laser.

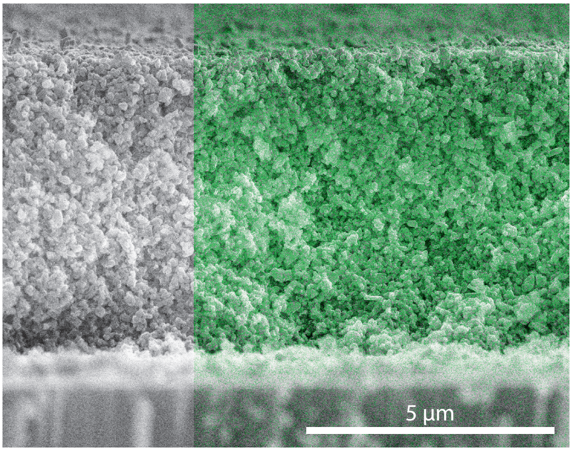

FIGURE M4.3: EDS map of a cross-sectioned, converted canvas. Left: SEM image showing the nanoparticles in the film. Right: elemental map overlay showing the presence of bromide (green) throughout the film, indicating conversion from top to bottom.

4.4.4 LED Fabrication

The stack used to fabricate the LED is ITO/PVK/perovskite/TPBi/LiF/Al. First, glass-ITO substrates were cleaned with sonication subsequently for 15 minutes in detergent in deionized water, acetone, and isopropanol, followed by oxygen plasma for 15 minutes at 100 W. The hole injection layer is prepared by dissolving 9 mg of Poly(9-vinylcarbazole) powder in 1 ml of chlorobenzene, stirred overnight and then spun at 2000 rpm for 60 seconds with a ramp of 1000 rpm/s on the cleaned ITO substrates. The films were then annealed at 120 °C for 20 minutes. Second, the $PbCO_3$ canvas was created and converted to perovskite: after 1 second of plasma cleaning of the PVK surface, 150 µl of $PbCO_3$ dispersion (prepared as above, settled for 24 h) were drop cast onto the PVK film at 50 °C. The lead carbonate films were converted to perovskite by immersing them into a conversion ink for 30 seconds (0.16 mmol/ml FABr in anhydrous IPA) and drying them under N_2 flow. Finally, the films were taken into an evaporation chamber where 40 nm TPBi (0.1 Å/s), 1.2 nm LiF (0.1 Å/s), and 100 nm aluminum (1 Å/s) were sequentially deposited at a pressure of 10-7 mbar to serve as electron injection layer and cathode. Prior IV and EL characterizations, the devices were encapsulated using epoxy glue and glass coverslips.

4.4.5 LED Characterization

The top contact, as well as the ITO film, was segmented into six sections, which could be individually addressed. A custom software took care of recording the current density versus voltage behavior via a Keithley 2440. For the EL measurement, a continuous voltage of 10 V was applied while simultaneously capturing the emitted light with a fiber-coupled spectrometer (Ocean Optics). To enhance the light collection, a 30 mm lens was mounted above the device to collect the emission and focus it into the fiber towards the spectrometer.

4.5 Appendix

4.5.1 Photoluminescence of Formamidinium Lead Halide Perovskites

Formamidinium lead halide perovskites can be created via ion exchange of $PbCO_3$ with formamidinium halide inks. Figure A4.1 shows typical PL spectra of blue-, green-, and red-emitting perovskites.

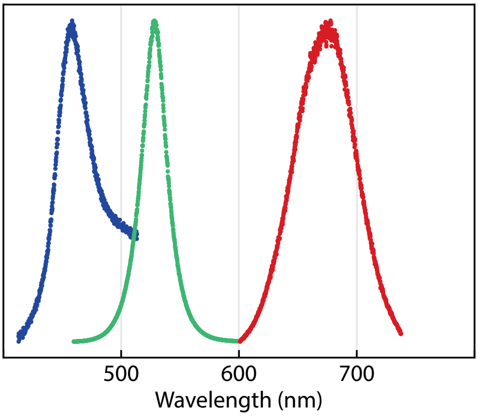

FIGURE A4.1: Normalized photoluminescence spectra of formamidinium lead halide perovskites created by ion exchange reaction of $PbCO_3$ with: blue: FACl-FABr (6:4); green: FABr, red: FABr-FAI (2:8).