

# ADVANCED MATERIALS

## Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.202005291

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

*Lukas Helmbrecht, Moritz H. Futscher, Loreta A. Muscarella, Bruno Ehrler, and Willem L. Noorduin\**

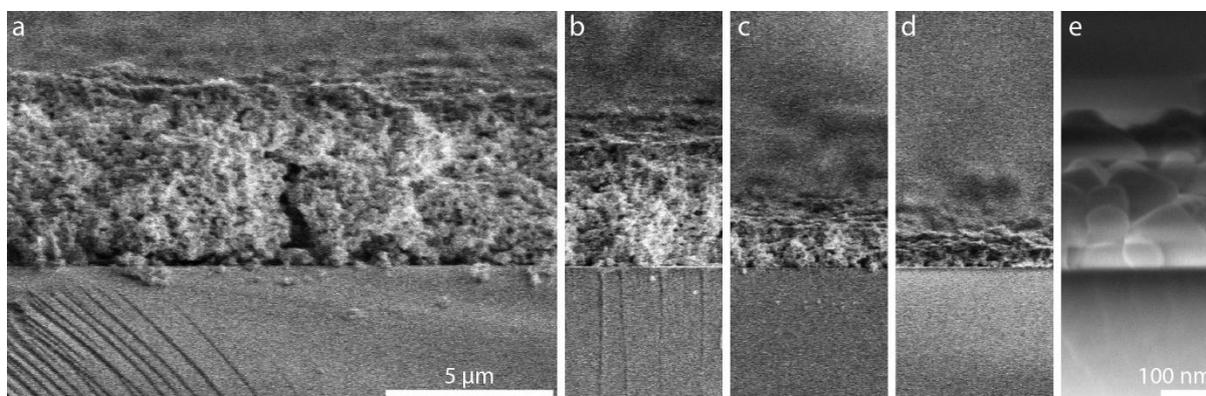
© 2021 Wiley-VCH GmbH

## Supporting Information

**Ion Exchange Lithography: Localized Ion Exchange Reactions for Spatial Patterning of Perovskite Semiconductors and Insulators***Lukas Helmbrecht, Moritz H. Futscher, Loreta A. Muscarella, Bruno Ehrler, Wim L. Noorduin\**Fabrication of lead-carbonate canvas

Lead carbonate powder (2 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  $\text{PbCO}_3/\text{ml}$  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  $\mu\text{L}$  of the  $\text{PbCO}_3/\text{MEOH}$  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 S1). 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 Figure S2g).

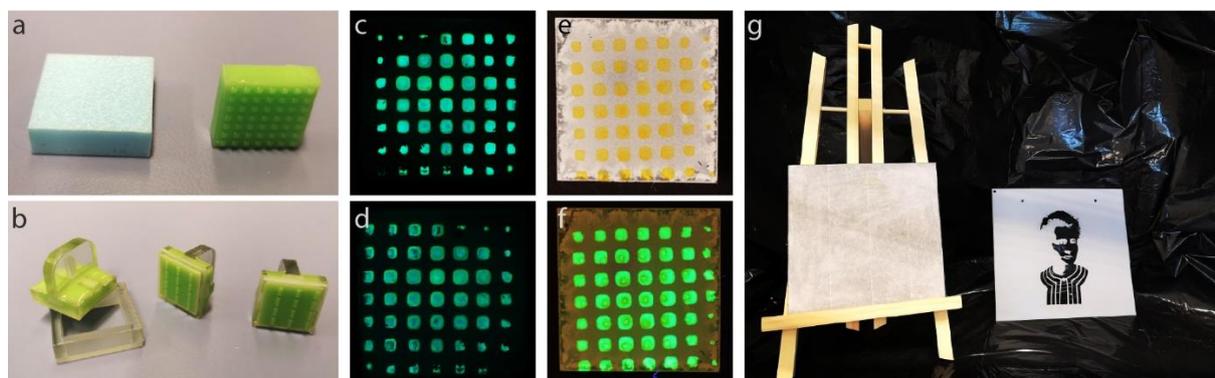


**Figure S1.** Lead carbonate nanoparticle films of decreasing thickness. a) 5  $\mu\text{m}$  film created with stock solution. b-e) Dilution of the dispersion allows for thinner films. Note the higher magnification in e).

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 S2).

The conversion ink was prepared by dissolving 0.16 mmol methyl ammonium 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  $\mu\text{L}$  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  $\text{PbCO}_3$ , the stamp is gently pressed on the canvas, assuring sufficient contact pressure to transfer the ink without damaging the canvas.



**Figure S2.** 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) and g) perovskite pattern in daylight and with additional UV light, respectively. c) Setup for airbrush painting with a stencil.

#### IEL with micropatterned PDMS stamps

Poly(dimethyl)silane (PDMS) stamps with micropatterns were cast from SU8-Si masters using replica molding. The SU8-Si masters were prepared using standard photolithography methods. Subsequently, the surface of the SU8-Si master, containing a negative of the desired pattern, was chemically modified with silane groups. To this aim, the SU8-Si master was placed in a desiccator with two drops of a fluoroalkylsilane and put under reduced pressure for minimal 2 hours. Subsequently, the stamp was fabricated by casting poly(dimethyl)silane (Sylgard 184) on the silanized master. After curing at 65 °C for 2 hours, the PDMS stamp was carefully peeled off the master.

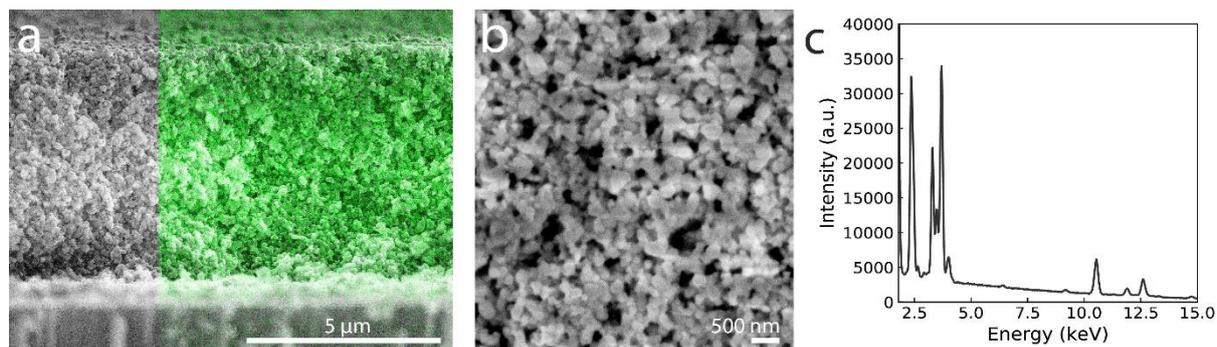
Ion exchange ink was carefully applied in the same manner as for the silicon stamps. The stamp was then first brought in contact with a sacrificial  $\text{PbCO}_3$  film to “pre-stamp” and remove excess ink before pressing it onto the lead carbonate canvas.

#### 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 2 and 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<sup>n</sup> energy dispersive X-ray spectrometer (Figure 2 and S3).

Photoluminescence was studied using a Witec alpha 300 in combination with a Thorlabs S1FC405 405nm laser.



**Figure S3.** a) 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. b) High resolution SEM image showing the morphology retention in a  $\text{PbCO}_3$  film exposed to FABr for 30 minutes. c) EDS spectrum of this film, showing the characteristic peaks of the glass substrate, lead, and bromide, allowing an analysis of the composition (25/75 at.% (Br/Pb)).

### 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  $\text{PbCO}_3$  canvas was created and converted to perovskite: after 1 second of plasma cleaning of the PVK surface, 150  $\mu\text{l}$  of  $\text{PbCO}_3$  dispersion (prepared as above, settled for 24h) 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  $\text{N}_2$  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 Al (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.

### Photoluminescence Quantum Yield

We characterize the photoluminescence quantum yield (PLQY) of the ion exchanged films with a custom-built setup. The details have been previously published (B. K. Patra *et al.* ACS Applied Materials & Interfaces 2020, 12, 31764). It is based on a Labsphere integrating sphere. The sample is placed inside the sphere and excited with a UV laser (Thorlabs, L405P20, 405 nm) which is modulated by optical chopper (Thorlabs, MC2000B-EC). Light leaving the integrating sphere is collected with a low-noise calibrated photodetector (Newport 818-SL) which is read out by an lock-in amplifier (Stanford Research Systems SR830) lock-in amplifier. The excitation and emission are measured separately, using a short pass filter (Thorlabs FESH0450) and long pass filter (Thorlabs FELH0450) in front of the photodetector, respectively. The PLQY ( $\eta$ ) is calculated as follows:

$$\eta = \frac{P_c - (1-A)P_b}{L_a A}, \quad \text{with} \quad A = \frac{L_b - L_c}{L_b} = 1 - \frac{L_c}{L_b}. \quad (1)$$

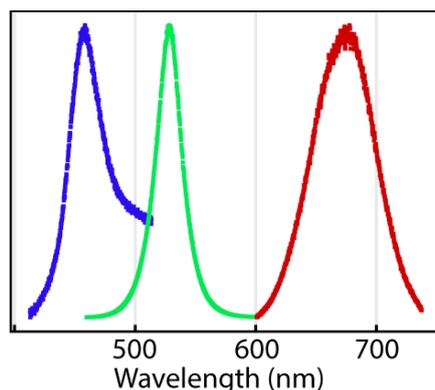
$P_c$  and  $P_b$  are the photoluminescence resulting from direct and indirect excitation of the sample.  $L_a$ ,  $L_b$ , and  $L_c$  are the laser light intensity, leaving the sphere, measured for an empty sphere, indirect excitation, and direct excitation of the sample, respectively.  $A$  is the absorbance of the sample.

#### 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.

#### Photoluminescence of Formamidinium Lead Halide Perovskites

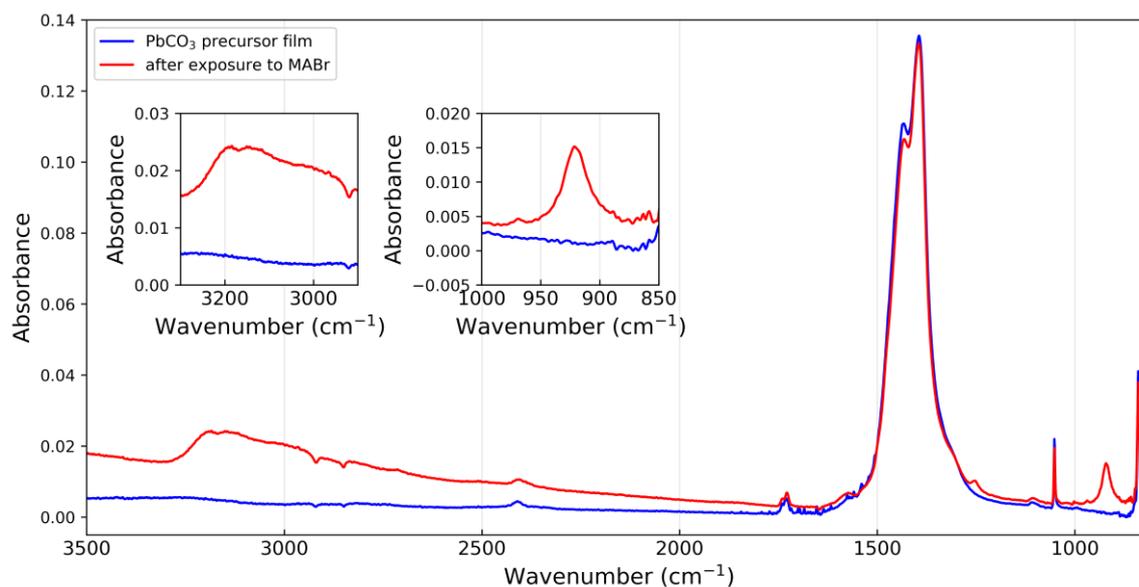
Formamidinium lead halide perovskites can be created via ion exchange of  $PbCO_3$  with formamidinium halide inks. Figure 7 shows typical PL spectra of blue-, green-, and red-emitting perovskites.



**Figure S4.** Normalized photoluminescence spectra of formamidinium lead halide perovskites created by ion exchange reaction of  $PbCO_3$  with: blue: FAcI-FABr (6:4); green: FABr, red: FABr-FAI (2:8).

#### IR spectroscopy analysis

We performed IR-spectroscopy studies on  $PbCO_3$  films before and after conversion to  $MAPbBr_3$  using a Bruker Vertex 80v FT-IR spectrometer. For these experiments, we deposited a thin film (0.5-1.0  $\mu m$ ) of  $PbCO_3$  nanoparticles on IR-transparent calcium fluoride substrates and measured under nitrogen atmosphere. The partially converted sample shows characteristic perovskite peaks (N-H stretch at 3200-3000  $cm^{-1}$ , and  $-CH_3$  rocking at 920  $cm^{-1}$ ) (Figure S5). However, no characteristic peaks of the expected side products  $H_2O$  (1650  $cm^{-1}$ ) and  $CH_3NH_2$  (2900  $cm^{-1}$ ), and the solvent IPA (2950  $cm^{-1}$ ) are found.



**Figure S5.** IR microscopy study of PbCO<sub>3</sub> film before and after partial conversion to MAPbBr<sub>3</sub>, insets show characteristic perovskite peaks: N-H stretch at 3200-3000 cm<sup>-1</sup>, and -CH<sub>3</sub> rocking at 920 cm<sup>-1</sup>. The characteristic CO<sub>3</sub> peaks of PbCO<sub>3</sub> at 1500-1300 cm<sup>-1</sup> overlap with the C-H bend of the perovskite.