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1 **TITLE:**
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3 Methylammonium Lead Halide Perovskite Films
4

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87 **KEYWORDS:**

88 Lead Halide Perovskite, Low-Pressure Vapor-Assisted Solution Process, Thin Film, Solar Cell,

90

91 **SHORT ABSTRACT:**

92 Here, we present a protocol for the synthesis of $\text{CH}_3\text{NH}_3\text{I}$ and $\text{CH}_3\text{NH}_3\text{Br}$ precursors and the
93 subsequent formation of pinhole-free, continuous $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ thin films for the application
94 in high efficiency solar cells and other optoelectronic devices.

95

96 **LONG ABSTRACT:**

97 Organo-lead halide perovskites have recently attracted great interest for potential applications
98 in thin-film photovoltaics and optoelectronics. Herein, we present a protocol for the fabrication
99 of this material via the low-pressure vapor assisted solution process (LP-VASP) method, which
100 yields ~19% power conversion efficiency in planar heterojunction perovskite solar cells. First, we
101 report the synthesis of methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) and methylammonium bromide
102 ($\text{CH}_3\text{NH}_3\text{Br}$) from methylamine and the corresponding halide acid (HI or HBr). Then, we describe
103 the fabrication of pinhole-free, continuous methylammonium-lead halide perovskite
104 ($\text{CH}_3\text{NH}_3\text{PbX}_3$ with $X = \text{I}, \text{Br}, \text{Cl}$ and their mixture) films with the LP-VASP. This process is based on
105 two steps: i) spin-coating of a homogenous layer of lead halide precursor onto a substrate, and
106 ii) conversion of this layer to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ by exposing the substrate to vapors of a mixture of
107 $\text{CH}_3\text{NH}_3\text{I}$ and $\text{CH}_3\text{NH}_3\text{Br}$ at reduced pressure and 120°C . Through slow diffusion of the
108 methylammonium halide vapor into the lead halide precursor, we achieve slow and controlled
109 growth of a continuous, pinhole-free perovskite film. The LP-VASP allows synthetic access to the
110 full halide composition space in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ with $0 \leq x \leq 3$. Depending on the composition of
111 the vapor phase, the bandgap can be tuned between $1.6 \text{ eV} \leq E_g \leq 2.3 \text{ eV}$. In addition, by varying
112 the composition of the halide precursor and of the vapor phase, we can also obtain $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$.
113 Films obtained from the LP-VASP are reproducible, phase pure as confirmed by X-ray
114 diffraction measurements, and show high photoluminescence quantum yield. The process does
115 not require the use of a glovebox.

116

117 **INTRODUCTION:**

118 Hybrid organic-inorganic lead halide perovskites ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $X = \text{I}, \text{Br}, \text{Cl}$) are a new class of
119 semiconductors that has emerged rapidly within the last few years. This material class shows
120 excellent semiconductor properties, such as high absorption coefficient¹, tunable bandgap², long
121 charge carrier diffusion length³, high defect tolerance⁴, and high photoluminescence quantum
122 yield^{5,6}. The unique combination of these characteristics makes lead halide perovskites very
123 attractive for application in optoelectronic devices, such as single junction^{7,8} and multijunction
124 photovoltaics^{9,10}, lasers^{11,12}, and LEDs¹³.

125

126 $\text{CH}_3\text{NH}_3\text{PbX}_3$ films can be fabricated by a variety of synthetic methods¹⁴, which aim at improving
127 the efficiency of this semiconducting material for energy applications¹⁵. However, optimization
128 of photovoltaic devices relies on the quality of the halide perovskite active layer, as well as its
129 interfaces with charge selective contacts (i.e. electron and hole transport layers), which facilitate
130 photocarrier collection in these devices. Specifically, continuous, pinhole-free active layers are
131 necessary to minimize shunt resistance, thereby improving device performance.

132

133 Among the most widespread methods for fabricating organo-lead halide perovskite thin films are
134 solution-based and vacuum-based processes. The most common solution process uses equimolar
135 ratios of lead halide and methylammonium halide dissolved in dimethylformamide (DMF),
136 dimethylsulfoxide (DMSO), or γ -butyrolactone (GBL), or mixtures of these solvents.^{2,16,17}
137 Precursor molarity and solvent type, as well as annealing temperature, time and atmosphere,
138 must be precisely controlled to obtain continuous and pinhole-free films.¹⁶ For example, to
139 improve surface coverage, a solvent-engineering technique was demonstrated to yield dense and
140 extremely uniform films.¹⁷ In this technique, a non-solvent (toluene) is dripped onto the
141 perovskite layer during the spinning of the perovskite solution.¹⁷ These approaches are usually
142 well suited for mesoscopic heterojunctions, which employ mesoporous TiO₂ as an electron
143 selective contact with increased contact area and reduced carrier transport length.

144
145 However, planar heterojunctions, which use selective contacts based on thin (usually TiO₂) films,
146 are more desirable because they provide a simple and scalable configuration that can be more
147 easily adopted in solar cell technology. Therefore, the development of organo-lead halide
148 perovskite active layers that show high efficiency and stability under operation for planar
149 heterojunctions may lead to technological advancements in this field. However, one of the main
150 challenges to fabricate planar heterojunctions is still represented by the homogeneity of the
151 active layer. A few attempts, based on vacuum processes, have been made to prepare uniform
152 layers on thin TiO₂ films. For example, Snaith and collaborators have demonstrated a dual
153 evaporation process, which yield highly homogenous perovskite layers with high power
154 conversion efficiencies for photovoltaic applications.¹⁸ While this work represents a significant
155 advancement in the field, the use of high vacuum systems and the lack of tunability of the
156 composition of the active layer limit the applicability of this method. Interestingly, extremely high
157 uniformity has been achieved with the vapor-assisted solution process (VASP)¹⁹ and modified low
158 pressure VASP (LP-VASP)^{6,20}. While the VASP, proposed by Yang and collaborators¹⁹, requires
159 higher temperatures and the use of a glove box, the LP-VASP is based on the annealing of a lead
160 halide precursor layer in the presence of methylammonium halide vapor, at reduce pressure and
161 relatively low temperature in a fumehood. These specific conditions enable access mixed
162 perovskite compositions, and fabrication of pure MAPbI₃, MAPbI_{3-x}Cl_x, MAPbI_{3-x}Br_x, and MAPbBr₃
163 can be easily achieved. Specifically, CH₃NH₃PbI_{3-x}Br_x films over the full composition space can be
164 synthesized with high optoelectronic quality and reproducibility^{6,20}.

165
166 Herein, we provide a detailed description of the protocol for the synthesis of organic-inorganic
167 lead halide perovskite layers via LP-VASP, including the procedure for synthesizing the
168 methylammonium halide precursors. Once the precursors are synthesized, formation of
169 CH₃NH₃PbX₃ films consists of a two-step procedure that comprises i) the spin-coating of the
170 PbI₂/PbBr₂ (or PbI₂, or PbI₂/PbCl₂) precursor on glass substrate or fluorine-doped tin oxide (FTO)
171 coated glass substrate with planar TiO₂, as electron transport layer, and ii) the low pressure
172 vapor-assisted annealing in mixtures of CH₃NH₃I and CH₃NH₃Br that can be finely adjusted
173 depending on the desired optical bandgap ($1.6 \text{ eV} \leq E_g \leq 2.3 \text{ eV}$). Under these conditions, the
174 methylammonium halide molecules present in the vapor phase slowly diffuse into the lead halide
175 thin film yielding continuous, pinhole-free halide perovskite films. This process yields a two-fold
176 volume expansion from the starting lead halide precursor layer to the completed organic-

177 inorganic lead halide perovskite. The standard thickness of the perovskite film is about 400 nm.
178 It is possible to vary this thickness between 100-500 nm by changing the speed of the second spin
179 coating step. The presented technique results in films of high optoelectronic quality, which
180 translates to photovoltaic devices with power conversion efficiencies of up to 19% using a
181 Au/spiro-OMeTAD /CH₃NH₃PbI_{3-x}Br_x/compact TiO₂/ FTO/glass solar cell architecture.²¹

182 183 **PROTOCOL:**

184
185 Caution: Please consult all relevant material safety data sheets (MSDS) before use. Several of the
186 chemicals used in these syntheses are acutely toxic, carcinogenic, and toxic to reproduction.
187 Implosion and explosion risks are associated with the use of a Schlenk line. Please make sure to
188 check the integrity of the glass apparatus before performing the procedure. Incorrect use of the
189 Schlenk line in association with a liquid nitrogen cold trap may result in condensation of liquid
190 oxygen (pale blue) that can become explosive. Please ensure to receive appropriate on the job
191 training by experts before using vacuum-systems, Schlenk lines, and cryogenic liquids. Please use
192 all appropriate safety practices when performing the synthesis including the use of engineering
193 controls (fume hood) and personal protective equipment (safety glasses, gloves, lab coat, full
194 length pants, closed-toe shoes). All of the following procedures described below are performed
195 in a fume hood in air, unless stated differently.

196 197 **1. Preparation of methylammonium halide**

198 1.1) To a 250 mL round bottom flask equipped with a stir bar, add ethanol (100 mL) and
199 methylamine (190 mmol, 16.5 mL, 40%_{wt} in H₂O), and cool the flask to 0 °C with an ice bath.

200 1.2) While the methylamine solution has been stirring for about 5 min at 600 revolution per
201 minute (rpm), add HI (76 mmol, 10 mL, 57%_{wt} in H₂O) or HBr (76 mmol, 8.6 mL, 48%_{wt} in H₂O)
202 dropwise, and seal the flask with a septum.

203 1.3) Allow the reaction to stir for 2 h at 0 °C.

204 1.4) Remove the reaction flask from the ice bath and evaporate the solvent and unreacted
205 volatile components at reduced pressure (~50 Torr) with a rotary evaporator equipped with a
206 water bath at 60 °C for 4 h.

207 1.5) To recrystallize the resulting solid, add warm (~50 °C) ethanol (100 mL) and dissolve the
208 residual material.

209 1.6) Slowly add diethyl ether (200 mL) to induce crystallization of a white solid.

210 1.7) Vacuum filter the mixture over a coarse 50 mm glass frit filter.

211 1.8) Recover the supernatant and add diethyl ether (200 mL) to induce additional crystallization
212 of white solid. Vacuum filter the mixture over a second coarse 50 mm glass frit filter.

213 1.9) Combine the white solids on a coarse 50 mm glass frit filter and, while vacuum filtering, wash
214 three times the resulting powder with diethyl ether (~30 mL each time).

215 1.10) Dry the white solid under vacuum. This procedure yields (58.9 mmol, 9.360 g, 77%) of
216 methylammonium iodide (MAI) and (55.5 mmol, 6.229 g, 73%) of methylammonium bromide
217 (MABr).

218 1.11) Store in the dark and in a desiccator at room temperature in order to minimize
219 decomposition over time.

220

221 2. Preparation of methylammonium lead halide ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$) thin films^{6,20}

222 2.1) Pre-conditioning of the Schlenk tube

223 2.1.1) Load a 50 mL Schlenk tube (diameter 2.5 cm) with 0.1 g of methylammonium halide. To
224 prevent the chemicals sticking to the walls of the test tube, use a weighing paper cylinder to
225 transfer the methylammonium halide into the tube.

226

227 Note: The final ratio of I/(I+Br) in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ is determined by the methylammonium halide
228 composition in the test tube. For example, to achieve 30% I content, the Schlenk tube is loaded
229 with 0.03 g MAI and 0.07 g MABr. Actual obtained compositions may vary with experimental
230 setup, so calibration of the synthesis conditions to yield specific target compositions is necessary.
231 In the present case, this was accomplished by measuring halide content in the synthesized films
232 via energy dispersive X-ray spectroscopy (EDX).

233

234 2.1.2) Use a Schlenk line equipped with a rotary pump to connect and evacuate the tube. Adjust
235 the pressure to 0.185 Torr. Then, immerse the test tube in a silicone oil bath pre-heated to 120°C,
236 with a magnetic stirrer (600 rpm) for 2 h (pre-conditioning of the Schlenk tube). This step allows
237 for sublimation of the methylammonium precursor along the sides of the Schlenk tube.

238

239 Note: It is important to ensure the sublimation of the methylammonium precursor during the
240 two hours of pre-conditioning. A thin layer of methylammonium precursor will condense along
241 the sides of the Schlenk tube to cover the lower half of the tube. If the pressure of the Schlenk
242 line and the temperature of the oil bath are correct, and you do not observe sublimation of the
243 methylammonium precursor or you observe that is happening too fast, you should use fresh
244 methylammonium precursor.

245

246 2.1.3) Remove Schlenk tube from the oil bath and leave methylammonium halide under an
247 overpressure of flowing N_2 to avoid moisture intake.

248

249 2.2) Substrate preparation

250

251 2.2.1) Sonicate one substrate (glass or FTO coated glass, 14 x 16 mm²) with water (~ 3 mL)
252 containing detergent for 15 min in a test tube (diameter 1.5 cm and height 15 cm) at 35 KHz.

253
254 2.2.2) Discard the detergent/water by rinsing with ultrapure water (~10 mL) 5 times.
255
256 2.2.3) Discard the ultrapure water, add acetone (~3 mL), and sonicate for 15 min at 35 KHz.
257
258 2.2.4) Discard the acetone, add isopropanol (~3 mL), and sonicate for 15 min at 35 KHz.
259
260 2.2.5) Discard the isopropanol, recover the substrate from the test tube with tweezers, and dry
261 it with a N₂ gun for 15 s.
262
263 2.2.6) Deposit TiO₂ compact layer (100 nm) on FTO glass substrates by electron beam evaporation
264 at a substrate temperature of 350 °C, and a deposition rate of 0.5 Å/s using substrate rotation.²¹
265
266 2.3) Preparation of the lead halide precursor solution
267
268 2.3.1) For the preparation of MAPbI_{3-x}Br_x (0 < x < 3), dissolve PbI₂ (0.8 mmol, 0.369 g) and PbBr₂
269 (0.2 mmol, 0.073 g) in 1 mL DMF to achieve a final concentration of 0.8 M of PbI₂ and 0.2 M of
270 PbBr₂. Heat for 5 minutes at 110 °C, and then sonicate for 1 min at 35 KHz to fully dissolve the
271 precursor.
272
273 2.3.1.1) For the preparation of pure iodine or bromine films, dissolve PbI₂ (1 mmol, 0.461 g) or
274 PbBr₂ (0.8 mmol, 0.292 g) in 1 mL DMF, to achieve a final concentration of 1 M and 0.8 M,
275 respectively. Heat for 5 minutes at 110 °C, and then sonicate for 1 min at 35 KHz to fully dissolve
276 the precursor.
277
278 2.3.1.2) For the preparation of chlorine-doped methylammonium lead iodide perovskite films,
279 dissolve PbI₂ (0.8 mmol, 0.369 g) and 0.2 M PbCl₂ (0.2 mmol, 0.056 g) in 1 mL DMF, to achieve a
280 final concentration of 0.8 M of PbI₂ and 0.2 M of PbCl₂. Heat for 5 minutes at 110 °C, and then
281 sonicate for 1 min at 35 KHz to fully dissolve the precursor.
282
283 2.3.2) Filter the precursor solution with a 0.2 μm polytetrafluorethylene (PTFE) filter.
284
285 2.4) Lead halide deposition
286
287 2.4.1) Pre-heat the precursor solution on a hot plate set to 110 °C for 5 min.
288
289 2.4.2) With a micropipette, drop 80 μL of the pre-heated lead halide precursor solution onto non-
290 rotating substrate (glass or TiO₂ deposited on FTO coated glass; 14x16 mm² size). Spin at 500 rpm
291 for 5 s with an acceleration rate of 500 rpm s⁻¹, and 1500 rpm for 3 min with an acceleration rate
292 of 1500 rpm s⁻¹.
293
294 2.4.3) In a fumehood, dry precursor film for 15 min at 110 °C on a hot plate under flowing N₂. A
295 crystalizing dish is used and placed over the substrate to allow the precursor to dry in a N₂
296 atmosphere.

297
298 Note: To vary the thickness of the resulting perovskite film, the speed of the second spin-coating
299 step can be varied from 1200 to 12000 rpm to achieve film thickness in the range of 500 to 100
300 nm. To further decrease the film thickness, diluted precursor solution can be used.

301 302 2.5) Vapor-assisted annealing

303
304 2.5.1) Load sample into the Schlenk tube (prepared according to instructions in section 2.1.2).
305 Adjust the pressure to 0.185 Torr.

306
307 Note: The sample sits in the test tube above the methylammonium halide without being in direct
308 contact with it. To slow down incorporation of methylammonium, the lead halide surface is
309 oriented to face away from the methylammonium halide.

310
311 2.5.2) Immerse the Schlenk tube loaded with the sample in silicone oil bath heated to 120 °C for
312 2 h.

313
314 2.5.3) Take out the sample and quickly rinse it by dipping it in a beaker containing isopropyl
315 alcohol. Immediately dry the rinsed sample with a N₂ gun.

316
317
318 Note: To prepare pure CH₃NH₃PbI₃ use PbI₂ as the halide precursor and pure methylammonium
319 iodide in the vapor-assisted annealing step. To prepare CH₃NH₃PbBr₃ use PbBr₂ as the halide
320 precursor and pure methylammonium bromide in the vapor-assisted annealing step.

321 322 **REPRESENTATIVE RESULTS:**

323 Proton nuclear magnetic resonance (NMR) spectra were taken after the methylammonium halide
324 synthesis to verify the molecule purity (Figure 1). Scanning electron microscopy (SEM) images
325 were acquired before and after vapor annealing (Figure 2) to characterize the morphology and
326 the homogeneity of both the mixed lead halide precursor and the CH₃NH₃PbI_{3-x}Br_x films. X-ray
327 diffraction (XRD) patterns were collected to confirm phase purity and conversion of lead halide
328 to CH₃NH₃PbI_{3-x}Br_x (Figure 3).

329
330 [Place Figure 1 here]

331
332 Methylammonium bromide and methylammonium iodide may be readily characterized by ¹H
333 NMR (Figure 1). The chemical shift of the methyl group is a sharp singlet centered at δ 2.35 ppm
334 (3H) for the MABr, and δ 2.37 ppm (3H) for MAI. The ammonium shift is a broad singlet centered
335 at δ 7.65 ppm (3H), and δ 7.45 ppm (3H) for MABr and MAI respectively. The difference in
336 chemical shift of the two methylammonium halides is due to the different halide
337 electronegativities, which affect (de)shielding of the protons present in the molecules. These
338 chemical shifts are consistent with previously reported spectra^{22,23}.

339
340 [Place Figure 2 here]

341
342 Figure 2 (a,b) shows the homogeneous morphology of the lead halide precursor that is
343 subsequently converted to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ in mixtures of methylammonium iodide and bromide
344 (c-h). The resulting perovskite films are continuous, pinhole-free with grain sizes up to 700 nm.
345 The standard thickness of the perovskite film is about 400 nm, which is obtained by spin coating
346 1 M lead halide precursor solution at a speed of 1500 rpm. The thickness can be changed by
347 varying the rotational speed, with higher speeds yielding thinner films and *vice versa*.
348 Interestingly, the conversion from the lead halide precursor layer to the resulting lead halide
349 perovskite results in an approximate two-fold volume expansion.

350
351
352
353 The temperature of 120 °C for the vapor phase anneal is chosen such that methylammonium
354 halide sublimates, diffuses into the lead halide film, and the equilibrium between
355 methylammonium halide vapor and solid $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ is in favor of the perovskite phase. In a
356 previous study, we showed that annealing at 100 °C resulted in largely incomplete conversion to
357 the perovskite phase and that device performance was best when synthesis was performed at
358 120 °C instead of 150 °C.²⁰ The phase characterization of precursor and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films on
359 FTO glass substrates by XRD is presented in Figure 3a. The lead halide precursor (0.8 M PbI_2 and
360 0.2 M PbBr_2) shows PbI_2 phase with its main peak at approximately 12.7°. $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films
361 are phase pure and do not contain residual PbI_2 phase. The $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ XRD peaks exhibit a
362 systematic shift to higher angles due to gradual replacement of the larger I atoms by smaller Br
363 atoms leading to a decrease in lattice constant from $\sim 6.29 \text{ \AA}$ ($x = 0$) to $\sim 5.93 \text{ \AA}$ ($x = 3$)².

364
365 [Place Figure 3 here]

366
367 The picture of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films (Figure 3b) illustrates the gradual incorporation of Br,
368 resulting in a band gap increase from 1.6 eV to 2.3 eV, and thus the change in visible appearance
369 (left, pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ to right, pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$). The gradual increase of bandgap has been
370 shown by photoluminescence measurements, which were previously reported on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$
371 films with high optoelectronic quality over the full composition space.⁶

372
373 **Figure Legends:**

374 **Figure 1: Nuclear magnetic resonance spectra.**

375 a) ^1H NMR of MABr in DMSO-d₆. Peaks at δ 7.65 (br s, 3H) and 2.35 (s, 3H) ppm confirm the
376 identity of the molecule.²² b) ^1H NMR of MAI in DMSO-d₆. Peaks at δ 7.45 (br s, 3H) and 2.37
377 (s, 3H) ppm confirm the identity of the molecule.²³ The peaks at 2.50 and 3.33 ppm are due to
378 residual DMSO and water.

379
380 **Figure 2: Conversion of lead halide precursor to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$.** SEM images of the mixed
381 halide precursor (top row) and representative SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films annealed in
382 100%, 50%, and 30% methylammonium iodide. The faceted films are pinhole free, and show grain
383 sizes up to 700 nm (a, c, e, g: scale bar 5 μm ; b, d, f, h: scale bar 1 μm).

384

385 **Figure 3: Phase analysis and full composition spectrum $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films.** a) XRD patterns
386 of lead halide precursor showing PbI_2 phase, and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films with decreasing iodine
387 content. The magnified pattern clearly depicts the shift of the (110) peak position towards larger
388 diffraction angles upon Br incorporation. b) Picture of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films with gradual
389 incorporation of Br (left to right: pure $\text{CH}_3\text{NH}_3\text{PbI}_3$, 90%, 80%, 70%, 50%, 40%, 30%, 20%, 10%,
390 and pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$).

391

392 **DISCUSSION:**

393

394 In order to fabricate highly efficient organo-lead planar perovskite heterojunctions, the
395 homogeneity of the active layer is a key requirement. With respect to existing solution^{2,16,17} and
396 vacuum-based^{18,19} methodologies, our process is remarkably amenable to composition tunability
397 of the active layer that can be synthesized over the full $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ composition space with
398 high optoelectronic quality and reproducibility.^{6,20} In addition, this process allows for the use of
399 reduced pressure and relatively low temperature in a fumehood without requiring the use of a
400 glove box or high vacuum deposition.

401

402 While LP-VASP is highly reproducible and no modification to the protocol should be necessary, it
403 is noted that the actual Br/(Br+I) composition in the film may be slightly lower than the initial
404 composition of the Schlenk tube. To address this issue, it is critical to measure the halide content
405 via EDX in the final film as well as to confirm the perovskite structure via XRD, in order to perform
406 a calibration of the synthetic conditions yielding specific target compositions with respect to the
407 utilized experimental setup.

408

409 In addition, there are a few useful recommendations that can ensure the correct reliability of our
410 process. The quality of the starting materials is particularly important. Storing of both the organic
411 (MAX) and inorganic (PbX_2) precursors in a desiccator under nitrogen atmosphere and controlled
412 humidity is instrumental to ensure reproducibility in the synthesis. In addition, the organic
413 precursors need to be very clean and all the traces of starting materials should be removed with
414 careful washing.

415

416 We have demonstrated the synthesis of methylammonium halide and the subsequent
417 transformation of lead halide precursors to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ in mixtures thereof, resulting in
418 smooth, pinhole free films that exhibit good optoelectronic quality. With respect to previous
419 methods,^{2,16-19} this synthetic protocol is versatile and amenable to be adapted in different
420 laboratories because it is easily carried out in a fumehood. In addition, LP-VASP allows for facile
421 accessibility of different organo-lead halide perovskite composition and tuning of the band gap.

422

423 The presented film fabrication method provides superior morphology control as compared to
424 pure solution coating methods, yielding highly efficient planar perovskite heterojunction solar
425 cells. Because of the low processing temperature and of the use of standard equipment available
426 in most laboratories (i.e. fumehoods and Schlenk lines), this methodology is especially suitable
427 to fabricate single as well as multijunction solar cells, light emitting diodes, and lasers. We are
428 currently developing a process that allows to deposit large ($>2 \text{ cm}^2$) area continuous perovskite

429 thin films.

430

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437

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439 The authors have nothing to disclose.

440

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