MATERIALS SCIENCE

Inch-sized high-quality perovskite single crystals by suppressing phase segregation for light-powered integrated circuits

Yucheng Liu^{1,2}, Yunxia Zhang¹, Xuejie Zhu¹, Zhou Yang¹, Weijun Ke², Jiangshan Feng¹, Xiaodong Ren¹, Kui Zhao¹, Ming Liu³, Mercouri G. Kanatzidis²*, Shengzhong (Frank) Liu^{1,4,5}*

The triple-cation mixed-halide perovskite ($FA_xMA_yCs_{1-x-y}$)Pb(I_zBr_{1-z})₃ (FAMACs) is the best composition for thin-film solar cells. Unfortunately, there is no effective method to prepare large single crystals (SCs) for more advanced applications. Here, we report an effective additive strategy to grow 2-inch-sized high-quality FAMACs SCs. It is found that the judiciously selected reductant [formic acid (FAH)] effectively minimizes iodide oxidation and cation deprotonation responsible for phase segregation. Consequently, the FAMACs SC shows more than fivefold enhancement in carrier lifetimes, high charge mobility, long carrier diffusion distance, as well as superior uniformity and long-term stability, making it possible for us to design high-performance self-powered integrated circuit photodetector. The device exhibits large responsivity, high photoconductive gain, excellent detectivity, and fast response speed; all values are among the highest reported to date for planar-type single-crystalline perovskite photodetectors. Furthermore, an integrated imaging system is fabricated on the basis of 12 × 12 pixelated matrixes of the single-crystal photodetectors.

INTRODUCTION

Halide perovskite semiconductors have demonstrated rapid progress in photovoltaic and optoelectronic applications because of their broadly tunable compositions [APbX₃, $A = Cs^+$, $CH_3NH_3^+$ (methylammonium) or MA⁺), or CH(NH₂)₂⁺ (formamidinium or FA⁺); $X = Cl^{-}$, Br⁻, I⁻, or mixture thereof (1-4), achieved using simple processing approaches, strong light absorption (5, 6), large mobilities (7, 8), and long carrier diffusion lengths (9, 10). For photovoltaic application, the power conversion efficiency of single-junction perovskite solar cells has now reached 25.5% (11, 12). Thus, halide perovskite solar cells are the fastest-growing photovoltaic technology to date. Currently, the most efficient perovskite solar cells were based on polycrystalline perovskite thin films (13, 14). However, the massive amorphous or low crystallinity grain boundaries in the polycrystalline thin films are proven to be the main root cause for the low thermal decomposition temperature and pathways for ion migration, two major reasons leading to poor stability and notorious J-V (15, 16). Compared to polycrystalline thin films, perovskite single crystals (SCs), essentially free of grain boundary, have shown markedly enhanced optoelectronic performance, including longer carrier diffusion length (~10 µm) (17-19), lower trap densities (~10⁹ to 10¹¹ cm⁻³) (20, 21), higher carrier mobilities (~ $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (7, 22), extended absorption spectrum (6, 23), and suppressed ion migration effect (17, 24), which guarantee superior device performance with improved stability while maintaining high solar cell efficiency. Thus far, the solution-grown

Copyright © 2021 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

perovskite SCs using single-cation MAPbX₃ (X = Cl, Br, and I) (25, 26), FAPbX₃ (4, 27), and CsPbX₃ (1, 28) and dual-cation FA_xMA_{1-x}PbX₃ (29, 30), FA_xCs_{1-x}PbX₃ (31), and MAPb_xSe_{1-x}X₃ (32) have been well studied. The perovskite SCs can also be used as inexpensive solidstate broadband and narrowband photodetectors operating in the ultraviolet–visible–near-infrared (UV-vis-NIR) regions, x-ray detectors, or even gamma detectors. For a photodetector, one of the most important figures of merit is the specific detectivity (D^*), which characterizes the lowest light intensity it is able to detect with certainty. The specific detectivity is determined by the responsivity and dark noise current of the photodetector (33). Therefore, it is imperative to design and synthesize high-quality materials with low trap-state density to achieve suppressed dark current, high photon absorption, and long carrier diffusion length for best possible photoresponsivity.

While the original development started with single-cation MAPbI₃ (12), it is further transitioned to develop more stable and higherefficiency perovskite materials. By substituting MA with FA, the equally interesting α-FAPbI₃ perovskite is harvested, but unfortunately, in ambient conditions, α -FAPbI₃ is thermodynamically unstable because the FA⁺ is too large for the perovskite cage and undergoes a phase transition to a yellow δ -FAPbI₃ perovskitoid phase (34). The structural instability of FAPbI3 was recently addressed by partial substitution of MA, Rb, and Cs for FA and Br for I (35, 36). Therefore, more recent efforts have been devoted to multiple-cation mixed-halide perovskites, which are relatively stable with suppressed ionic migration, reduced photovoltaic hysteresis, and record efficiency, as demonstrated by the incorporation of Cs/MA/Br ions into the FAPbI₃ perovskite to form triple-cation mixed-halide (TCMH) polycrystalline perovskite thin films with composition of $(FA_{0.8}MA_{0.15}Cs_{0.05})$ PbI_{2.55}Br_{0.45} (37). However, the composition and ratio, especially the Cs contents of the TCMH perovskites for the state-of-the-art devices reported by different research groups, are not consistent (38, 39). For the TCMH composition perovskites, phase segregation into yellow phases such as δ -CsPbI₃ and δ -FAPbI₃ are often observed during the crystallization process (40, 41). The existing yellow phases in

¹Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology; Institute for Advanced Energy Materials; School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China. ²Department of Chemistry, Northwestern University, Evanston, IL 60028, USA. ³School of Microelectronics, Xi'an Jiaotong University, Xi'an 710049, China. ⁴Dalian National Laboratory for Clean Energy; Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China. ⁵University of the Chinese Academy of Sciences, Beijing 100039, China.

^{*}Corresponding author. Email: m-kanatzidis@northwestern.edu (M.G.K.); szliu@ dicp.ac.cn (S.L.)

perovskites act as trapping or scattering centers that negatively affect the charge carrier mobility and carrier recombination dynamics deteriorating the optoelectronic performance of SCs. By analyzing the experimental results from crystal growth studies, the main reasons for the phase separation are as follows (Fig. 1A): First, iodide can be easily oxidized into I_2 and triiodide ions (I_3^- ions) under heating and illumination by the oxygen dissolved in solution (this oxidation process can be expressed as Eqs. 1 and 2); second, deprotonation of CH(NH₂)₂⁺ to CHNH₂NH and H⁺ (CH₃NH₃⁺ to CH₃NH₂ and H⁺) occurred upon heating, as described in Eqs. 5 and 6. The above oxidation and deprotonation processes effectively reduce the supersaturation concentrations of iodide ions (I⁻), MA⁺, and FA⁺ in the single-crystal growth solution, thus slowing down the rate of crystallization. In addition, the triiodide ions (I_3^-) with larger diameter may produce large hole-trapping centers during the growth of SCs, and I_2 in the solution would initiate chemical reaction (Eq. 2) with I^- to again form I_3^- , leading to imbalanced ratios of I^- , MA⁺, and FA⁺, likely favoring the yellow phases δ -CsPbI₃ and δ -FAPbI₃. Both the iodide ion vacancies and impurity phases in SCs degrade the crystalline quality and deteriorate the optoelectronic performance of the SC devices.

RESULTS AND DISCUSSION

In this work, we show that the phase separation can be eliminated by suppressing the oxidation and deprotonation processes. On the basis of Fig. 1A, a chemically reducing reactant is expected to help suppress the oxidation and deprotonation reaction mentioned above. In this regard, formic acid (HCOOH or FAH) is selected, as it is readily soluble in the solution. It is of ideal redox potential to reduce only I_2 molecules and I_3^- ions without affecting other chemicals in



Fig. 1. Mechanism of phase separation suppressed by formic acid to TCMH perovskite single-crystal growth from FAMACs solution. (A) lodide oxidation, reduction reaction, and deprotonation/protonation in single-crystal growth solution. (B) Suppressed phase segregation in TCMH perovskite single-crystal growth by adding formic acid. (C) Phase segregation in TCMH perovskite single-crystal growth without adding formic acid.

the growth solution. Moreover, its reaction product is CO_2 that escapes from the solution without any contamination. More specifically, HCOOH eliminates undesirable iodide oxidation on the basis of the following reactions (see Eqs. 3 and 4 in Fig. 1) (42)

$$HCOO^{-} + 2I^{0} \rightarrow 2I^{-} + H^{+} + CO_{2}\uparrow$$
$$HCOO^{-} + I_{3}^{-} \rightarrow 3I^{-} + H^{+} + CO_{2}\uparrow$$

The FAH can reduce I^0 to I^- in the single-crystal growth solution, wherein the formed H⁺ simultaneously inhibits the deprotonation of CH(NH₂)₂⁺ to CHNH₂NH and H⁺ (Eq. 7). Furthermore, the above reactions have no influence on solution volume; hence, the concentration of all relevant reactants in the solution is kept unchanged, and the designed stoichiometric ratio is maintained. Here, we report the successful growth of TCMH perovskite SCs with the state-ofthe-art composition of FA_{0.9}Cs_{0.05}MA_{0.05}PbI_{2.7}Br_{0.3} (FAMACs). We demonstrate that, with FAH addition in the precursor solution, purephase and high-quality FAMACs SCs can be obtained (Fig. 1B). In contrast, the yellow phase like δ -CsPbI₃, δ -FAPbI₃, and FAMACs SCs are crystalized simultaneously but separately in solution (Fig. 1C).

To investigate the effect of FAH on the growth of FAMACs SCs, we begun by adding different concentrations (0, 1, 2, 3, and 5% in volume) of FAH in the precursor solution [FAMACs in γ butyrolactone (GBL)]. The solution was prepared by dissolving stoichiometric FAI, MABr, CsBr, PbI₂, and PbBr₂ in GBL at room temperature (ca. 21°C), forming a transparent bright yellow solution with concentration of 1.2 M, as shown in Fig. 2A. Then, the solutions were transferred to an oven and the temperature was increased to 60°C. After heating the solutions at 60°C for 5 hours, the temperature was slowly increased from 60° to 95°C with a slow ramp rate of 5°C/hour. Then, after continuously heating the solution at 95°C for 48 hours, a progressively darker color was observed until it turned reddish brown as the FAH concentration decreases (5, 3, 2, 1, and 0% FAH), as shown in Fig. 2A (top). This gradual color change is attributed to the formation of I₂ and I₃⁻ ions. When the heating process is carried out in a glovebox (in the absence of oxygen), the oxidation markedly decreases, as indicated by the stable bright yellow color (fig. S1), highlighting the role of oxygen in stimulating the oxidation reaction to form triiodide. Accordingly, growing the SCs under vacuum or a nitrogen flow might be a good choice. However, this is a relatively costly suboptimal option. In addition to oxygen, heating and illumination will also promote the oxidation of iodide and the deprotonation of amine ions. Instead, we use FAH as a powerful reducing agent to inhibit the oxidation and deprotonation.

Besides the color change of the solution, the number of crystals formed at the bottom of the container also increases as the concentration of FAH increases. As shown in Fig. 2A (bottom), it seems that adding 1% FAH is effective to reduce the amount of Γ ions being oxidized to I_3^- ions, as evidenced by the color change of the solution. Unfortunately, under these conditions, we do not observe any crystallization, even after 48 hours of heating. However, in the case of FAH >1%, several SCs formed at the bottom of the container, and the higher the concentration of FAH, the more SCs were formed. This indicates that FAH not only is a typical reducing agent but also can promote the crystallization for this perovskite system. To determine the optimal FAH concentration for the FAMACs SC growth, 2, 3, 4, and 5% FAH was separately added into four precursor solutions and heated at 95°C. As shown in Fig. 2B, after 54 hours, a small crystal and two



Fig. 2. Effect of formic acid addition to precursor solution and SC growth. (**A**) Photographs of the precursor solution with different concentrations of formic acid before and after heating at 95°C. (**B**) Photographs of SC growth in precursor solution with different concentrations of formic acid. (**C** and **D**) Photographs of the FAMACs SCs grown in precursor solution without formic acid for about 10 days and with 2% formic acid for about 27 days, respectively. (**E**) Powder x-ray diffraction (XRD) patterns of ground powder from a large FAMACs SC grown in precursor solution with and without formic acid. (**F** and **G**) XRD 2θ scan on the top facet of FAMACs SC and high-resolution rocking curve of the (110) and (220) diffractions of FAMACs SC grown in precursor solution with and without formic acid. a.u., arbitrary units. Photo credit: Yucheng Liu, Shaanxi Normal University.

big crystals formed in the solution with 2% FAH addition. In the case of 3% FAH, there were 11 smaller crystals formed. By increasing the FAH concentration to 4%, about 50 crystals were harvested. Further increasing the FAH concentration to 5% produced several hundred crystals. Meanwhile, when the concentration was raised to 3%, multiple smaller crystals formed and attached to each other. By systematically optimizing the concentration of FAH, we concluded that for the reaction condition used, the optimal concentration is at 2%.

Note that, by increasing the temperature to 105°C, crystals can eventually be obtained in the solution without addition of FAH. However, a large number of needle-like yellow crystals also appear in the container, as shown in fig. S2, and the following x-ray diffraction (XRD) test confirmed that these yellow crystals were mainly δ -CsPbI₃. As discussed above, the lack of Γ , MA⁺, and FA⁺ ions in the solution results in phase separation into the yellow phase δ -CsPbI₃. In addition, because of the appearance of the yellow needle-like crystals, the shape of the obtained SCs is irregular, their surface is not smooth, and there are still yellow crystals left on the black SCs,

indicating that the effect is initiated by a change in the solution composition with FAH addition. Figure S3 shows photographs of the large-sized FAMACs SCs before and after they were harvested from the growth solutions. The detailed growth process of the large-sized FAMACs SCs is provided in Materials and Methods. It is found that all of the large crystals adopt rhombic hexagonal dodecahedra geometry (Fig. 2D). The surface of the freshly grown crystals appears to be black and glossy. We note that Yang et al. (43) have reported the addition hypophosphorous acid (H_3PO_2) to prevent the oxidation of iodine in the crystallization of CH₃NH₃PbI₃ from GBL. However, we failed to obtain the FAMACs SCs in the limited experimental space that we explored without the addition of FAH (fig. S4). It seems that H₃PO₂ as the reducing agent may not be suitable in this TCMH perovskite system. H₃PO₂ effectively inhibits the oxidation of iodide ions, but it also hinders crystal growth from solution. The solution with no crystals when H₃PO₂ was added after heating for

as shown in Fig. 2C. However, on addition of 2% FAH to the initial

solution, we observe crystals of FAMACs SCs being formed at ~90°C,

48 hours at 95°C and the solution with crystals when FAH was added are shown in fig. S4.

Figure 2E compares the powder XRD patterns measured from the needle-like yellow crystals, the FAMACs SC grown in the solution with 0% FAH (0% FAH FAMACs SC), and the FAMACs SC grown in the solution with 2% FAH (2% FAH FAMACs SC). The XRD patterns demonstrate that the needle-like yellow crystals belong to δ -CsPbI₃ and δ -FAPbI₃, and the δ -CsPbI₃ peaks are observed in the 0% FAH FAMACs SC, but not in the 2% FAH FAMACs SC. The powder XRD of 2% FAH FAMACs SC shows very sharp Bragg peaks at 14.08°, 19.93°, 24.43°, 28.34°, 31.69°, 40.37°, and 42.98°, corresponding to the (100), (110), (111), (200), (210), (220), and (300) planes of the cubic crystal structure, respectively. To evaluate crystalline quality, the large SCs were directly used for XRD measurements. As shown in Fig. 2F, the x-ray 2θ scan on the maximal facet of a typical FAMACs SC shows only (110) and (220) diffraction peaks, suggesting wellstructured single-crystalline eminence. The higher diffraction intensity of the 2% FAH FAMACs SC demonstrates higher crystallinity than the 0% FAH FAMACs SC. We further measured the highresolution x-ray rocking curve of these two XRD peaks (Fig. 2G, left), with all showing very small full width at half maximum (FWHM), only 0.0202° and 0.0169°, respectively. Compared to the 2% FAH FAMACs SCs, the reference samples (0% FAH FAMACs SCs) show much inferior quality with the FWHM as wide as 0.0561° and 0.0353°, respectively. In short, the 2% FAH FAMACs SC is clearly better. In addition, the 2% FAH FAMACs SC is phase stable in ambient environment, as demonstrated by stable visual appearance, consistent XRD patterns (fig. S5), and x-ray photoelectron spectroscopy (XPS) (fig. S6) after more than 40 days of exposure in ambient environment. The better thermal stability was also observed from thermogravimetric analysis measurements (fig. S7). Compared with the 0% FAH FAMACs SC that decomposes at 294°C, the 2% FAH FAMACs SC is more stable with no signature of thermal decomposition until 310°C. Moreover, it is more stable than the most popular version of the MAPbI₃ and FAPbI₃ SC material (4). To verify that Cs and Br were successfully incorporated into the perovskite SCs, XPS measurements were performed on a large single crystal. As shown fig. S8, the resulting stoichiometry, as calculated from the relative peak areas, was found to be Cs:Pb:I:Br = 1:19.2:55.4:6.5, which is similar to the values of 1:20:54:6 in the SC growth solution. Furthermore, the ratio of I/Br was determined to be 8.67 \pm 0.61 by XPS measurements (fig. S9), consistent with the stoichiometric ratio of 9 in the growth solution. In contrast, the I/Br ratio in the 0% FAH FAMACs SCs is 5.26 ± 1.28 ; the noticeable iodide deficiency indicates that substantial amounts of I⁻ ions were oxidized during the crystallization process without FAH.

Optical properties of the FAMACs SC are shown in Fig. 3. The absorption spectra show that the crystal has a direct bandgap of 1.52 eV for 0% FAH FAMACs SC and 1.49 eV for 2% FAH FAMACs SC (Fig. 3A). From photoemission yield spectroscopy in air (PYSA) measurements, we estimated the valence band maxima (VBM) of FAMACs SCs to be situated at -5.46 and at -5.65 eV from the vacuum level for 0% FAH FAMACs SC and 2% FAH FAMACs SC, respectively (Fig. 3B). By combining these values with the corresponding optical band gaps, we deduce the conduction band minimum (CBM) to be at -3.94 eV for 0% FAH FAMACs SC and at -4.16 eV for 2% FAH FAMACs SC (Fig. 3C). In Fig. 3D, the steady-state photoluminescence (PL) reveals close to a twofold increase in PL intensity emanating from the 2% FAH FAMACs SC, a strong

indication for the reduction in the number of nonradiative recombination centers.

PL was used to study the stability of FAMACs SCs. Figure 3 (E and F) illustrates that the 0% FAH FAMACs SC shows no changes in the PL peak position, but its intensity increases by 39.5% from the initial value and then degrades to 22.7% from the maximum value in PL intensity under continuous 510-nm laser irradiation for 12 hours, as shown in Fig. 3G. Under the same conditions, the 2% FAH FAMACs SC sample retains the same PL peak and the intensity increases only 9.1% after 15 hours of irradiation. Furthermore, time-resolved PL measurements performed upon 510-nm excitation showed the average carrier lifetime of the 2% FAH FAMACs SC to be increased from 5.74 µs (0% FAH FAMACs SC) to 8.41 µs, and the recombination rate decreased by 46.5% (Fig. 3H). Therefore, strong PL enhancement indicates that the 2% FAH FAMACs SC suppresses the nonradiative recombination defects. The longer lifetime in the 2% FAH FAMACs SC indicates fewer defect states and less crystalline disorder as compared to the 0% FAH FAMACs SC. Note that both these two SCs show much longer lifetime than the single-cation FAPbI₃ SC (1.61 µs) and MAPbI₃ SC (0.38 µs), indicating the superior photoelectronic properties of the TCMH perovskite.

To confirm crystal uniformity, we also mapped the PL intensity and lifetime of SCs with 510-nm excitation (Fig. 3, I and J) and found that from the 2% FAH FAMACs SC, the intensity is higher, with longer lifetime and much more uniformity than the 0% FAH FAMACs SC. The separate PL intensity mapping and PL lifetime mapping are shown in fig. S10. Figure 3 (K and L) summarizes the PL intensity and lifetime measured on both types of crystals. It shows that the 2% FAH FAMACs SCs exhibit lower density of traps, as signposted by longer lifetime (8.74 ± 0.62 µs) and higher intensity (2.44 ± 0.59 × 10⁷ counts). In comparison, the 0% FAH FAMACs SCs show much higher traps, as evidenced by the shorter lifetime (6.39 ± 0.97 µs) and lower intensity (1.41 ± 0.15 × 10⁷ counts), which is about two times smaller than the 2% FAH FAMACs SCs. The excellent optical uniformity combined with the enhanced PL makes it a promising candidate for large-area optoelectronic applications.

Next, we investigated the key semiconducting parameters such as trap density (n_t) , charge mobility (μ) , and carrier diffusion length $(L_{\rm D})$ of the FAMACs SC. First, we estimated the relative dielectric constant (ε_r) from the capacitance-frequency measurement in the range of 100 Hz to 30 MHz (fig. S11A). Capacitance of the FAMACs SC was determined using an impedance analyzer (fig. S11B). The trap state densities (n_t) in the 2% FAH FAMACs SCs and 0% FAH FAMACs SCs were measured using the space charge-limited current (SCLC) method on hole-only and electron-only devices (Fig. 4, A to D), and their device structures are Au/FAMACs SC/Au and Ag/ phenyl-C60-butyric acid methyl ester (PCBM)/FAMACs SC/PCBM/ Ag, respectively, as inserted in the figures. Each current-voltage (I-V) curve exhibits three distinct regions, including ohmic region (red lines), a trap-filling region (purple lines), and a trap-free SCLC region (green lines). The hole and electron trap density were calculated using the equation $n_t = 2\varepsilon_0\varepsilon_r V_{TFL}/qL^2$ (44), where ε_0 , ε_r , q, and L are the vacuum permittivity, the relative dielectric constant, the elementary charge, and the thickness of the FAMACs SCs, respectively. As shown in Fig. 4E, the density of hole trap density decreases to $4.2 \pm 2.1 \times 10^9$ cm⁻³ after addition of 2% FAH in the precursor solution, which is about two orders of magnitude lower than the 0% FAH FAMACs SC devices $(2.6 \pm 1.3 \times 10^{11} \text{ cm}^{-3})$. The apparent density of electron traps also decreases from $5.1 \pm 2.2 \times 10^{11} \text{ cm}^{-3}$ to $1.6 \pm 0.5 \times 10^{10} \text{ cm}^{-3}$. These



Fig. 3. Optical characterization of the FAMACs SCs. (A) UV-vis-NIR absorption spectra and corresponding Tauc plots determining the extrapolated optical bandgap of 2% FAH FAMACs and 0% FAH FAMACs SC. (B) PYSA measurements showing VBM at –5.46 eV for 0% FAH FAMACs SC and –5.65 eV for 2% FAH FAMACs SC. (C) Band alignment of the 2% FAH FAMACs and 0% FAH FAMACs SC. Energy levels are expressed from the vacuum, which is set at zero. (D) Steady-state PL spectra of 2% FAH FAMACs and 0% FAH FAMACs SC excited at 510 nm. (E to G) Irradiation stability investigation of the 2% FAH FAMACs and 0% FAH FAMACs SC in air with ambient temperature and illumination under 510-nm laser. (H) Time-resolved PL comparison of the 0% FAH FAMACs SC, 2% FAH FAMACs SC, FAPbl₃ SC, and MAPbl₃ SC excited at 510 nm. (I and J) PL mapping comparison of the 0% FAH FAMACs SC and 2% FAH FAMACs SC. (K and L) Statistics of PL intensity and lifetime for both 2% FAH FAMACs SCs and 0% FAH FAMACs SCs.

results further demonstrate the dual suppression effect (iodide ion oxidation and cation deprotonation) of FAH. The hole and electron mobilities of 2% FAH FAMACs SCs and 0% FAH FAMACs SCs were measured by a time-of-flight method (45). The FAMACs SCs devices with the device structure of Au/FAMACs SC/PCBM/Au (fig. S12) were fabricated. The hole mobility of 2% FAH FAMACs SCs was found to be 219 ± 18 cm² V⁻¹ s⁻¹ (Fig. 4, F and H), much higher than that of the 0% FAH FAMACs SCs of 125 ± 21 cm² V⁻¹ s⁻¹ (Fig. 4, G and H). A comparable electron mobility of 197 cm² V⁻¹ s⁻¹ was measured for the 2% FAH FAMACs SCs (fig. S13).

The above results indicate that growing FAMACs SCs with FAH addition yields better crystals with improved optical and electronic properties. Using the μ value obtained from the time-of-flight method and the carrier lifetime τ from time-resolved PL, the diffusion length (L_D) can be calculated using $L_D = \sqrt{k_B T \mu \tau / q}$ (46), where k_B is the Boltzmann's constant, *T* is the temperature, and *q* is the elementary charge. In particular, the hole diffusion length L_D was derived to be 71 ± 5 µm for the 2% FAH FAMACs SCs and 46 ± 8 µm for the 0% FAH FAMACs SCs (Fig. 41), which is about five times longer than the values (0.2 to 12 µm) reported in single-cation perovskite SCs such as MAPbI₃ (26), MAPbBr₃ (26), FAPbI₃ (27), and FAPbBr₃ (46), demonstrating significantly better property of the present triplecation perovskite SCs. To confirm the higher quality of the FAMACs SCs, a detailed property parameter comparison between the published results and ours is shown in table S1.

With the above superior optoelectronic properties of TCMH FAMACs SC including high charge mobility, low trap density, long carrier diffusion length, and ambient stability, we fabricated lateral structure perovskite single-crystal solar cells using these SCs. As shown in fig. S14, the lateral structure perovskite single-crystal solar cell array is designed and fabricated on the 2% FAH FAMACs SC. Detailed analysis and characterization of the single-crystal solar cell array is shown in fig. S14. Even though the short-circuit current density (J_{sc}) of the integrated solar cells decreases slightly, but the total opencircuit voltage (V_{oc}) accumulates with the number of cells. Specifically, the V_{oc} is 0.74 ± 0.04 V for 1 solar cell, 2.11 ± 0.05 V for 3 solar cells. We noticed that this is an important strategy for obtaining large V_{oc} values because it can provide large bias voltage for special electronic devices such as integrated circuits.



Fig. 4. Trap density, charge mobility, and carrier diffusion length measurements. (A to D) Current-voltage curves of hole and electron devices of 2% FAH FAMACs SCs and 0% FAH FAMACs SCs, respectively. Solid lines are obtained by fitting the data. (E) Statistics of calculated trap density for 2% FAH SCs and 0% FAH FAMACs SCs. (F and G) Normalized time-of-flight hole charge transient curves of 2% FAH FAMACs SC and 0% FAH FAMACs SC devices under illumination (wavelength, 532 nm) with various bias voltages. (H) Statistics of measured hole mobility for 2% FAH FAMACs SCs and 0% FAH FAMACs SCs. (I) Statistics of calculated diffusion length for 2% FAH FAMACs SCs and 0% FAH FAMACs SCs.

As mentioned above, large bias can be easily obtained by integrating different numbers of lateral structure perovskite SC solar cells. For more choices, the output biases can be adjusted by the number of solar cells in series. Here, in this work, we advanced in fabrication the self-powered integrated circuits (SP-ICs) photodetector by combining the FAMACs SC solar cell array and the photodetector array. Figure 5A illustrates the connection of the SP-IC photodetector, in which the solar cells provide bias for photodetectors. As illustrated in Fig. 5B, the detector is integrated using 12 interdigit grid Au wires. The active channel dimension between two adjacent Au pads was 1.7 mm in length and 2 mm in width. The grid line was about 60 µm in width and 300 nm in thickness, and the gap between two grid lines is 40 μ m, giving an active device area of about 1.36 mm². As an efficient power supply, the solar cell should respond rapidly to the light. In Fig. 5C, the photocurrent rise speed to the light of the solar cell and detectors at a 5-V bias is compared. The response time is defined as the duration needed for the photo response to rise (decay) from 10% (90%) to 90% (10%). Under the same pulse laser light (460 nm), the rise time of the solar cell is 0.67 µs, which is faster

than the 2% FAH FAMACs SC detector (0.88 µs) and 0% FAH FAMACs SC detector (1.29 µs). These results indicate that the solar cell is an ideal candidate power supply for the integrated circuit photodetector. We further examined the response photocurrent of the 2% FAH FAMACs SC and 0% FAH FAMACs SC devices. Figure 5 (D and E) shows the photocurrent response powered by different solar cells and under illumination using 460-nm laser light with intensity ranging from 0.52 nW cm⁻² to 380 mW cm⁻². As expected from the high-quality 2% FAH FAMACs SC, the photocurrent is measured as high as 5.81×10^{-3} A under illumination (380 mW cm⁻²) and powered by 10 small cells integrated, more than five orders (4.92×10^5) of magnitude increase compared to the dark current of 1.18×10^{-8} A (fig. S15A). The dark current is a very important factor for applications in photodetectors and determines the detectivity, responsivity, and the signal-to-noise ratio. It is known that as the dark current mainly originates from material imperfections (such as traps), devices with fewer charge trap show lower dark current. Under the same illumination intensity, dark current and photocurrent of the 0% FAH FAMACs SC device with the same design were measured



Fig. 5. Fabrication and performance of self-powered perovskite SC detectors. (A and B) Photograph and schematic diagram of photodetector powered by integrated lateral structure perovskite SC solar cells. (C) TPC response of solar cell and detectors at a 5-V bias under illumination of 460-nm laser light. (D and E) Photocurrent response of the photodetector made on 2% FAH FAMACs SC and 0% FAH FAMACs SC under illumination (460 nm) at different light intensities and powered by different solar cell integrations. (F) Responsivity, photoconductive gain, and detectivity of the 2% FAH FAMACs SC photodetector under illumination at light power density of 0.52 nW cm⁻² and powered by different numbers of solar cells. Both active area and total area of the detector were used in the calculation. (G) TPC response of the 0% FAH FAMACs SC and 2% FAH FAMACs SC photodetector. (H) Frequency-dependent response of the 0% FAH FAMACs SC and 2% FAH FAMACs SC photodetector. Photo credit: Yucheng Liu, Shaanxi Normal University.

to be 1.97×10^{-7} and 4.69×10^{-3} A, respectively. The on/off ratio was calculated to be 2.38×10^4 (fig. S15B), more than 20 times smaller than the 2% FAH FAMACs SC device (4.92×10^5) . Note that the extremely low dark current demonstrated that the present 2% FAH FAMACs SC has good crystallinity and is grain boundary free, which suppresses the recombination of charge carriers and consequently lowers the dark current. Furthermore, the dark noise current measured directly by a dynamic signal analyzer is shown in fig. S16. It can be seen that the noise current is barely sensitive to frequency, indicating a negligible 1/f noise due to the minimized trap density and the absence of grain boundary in the 2% FAH FAMACs SC (22).

The key detector parameters such as responsivity (*R*), photoconductive gain (Gain), and detectivity (*D*) as a function of the incident light intensity were extracted and shown in fig. S17. Figure 5F shows *R*, Gain, and *D* for the photodetector based on the 2% FAH FAMACs SC under the biases provided by different numbers of solar cells. With the synergy of suppressed dark current and boosted photocurrent, the highest *R*, Gain, and *D* are calculated to be 598.6 A W⁻¹, 1613.8, and 6.7×10^{14} cm Hz^{1/2} W⁻¹ (Jones) under the lowest mea-

Liu et al., Sci. Adv. 2021; 7 : eabc8844 10 February 2021

sured incident light of 0.52 nW cm⁻². It is found that all of them are much higher than the values of the 0% FAH FAMACs SC detector of 424.6 Å W^{-1} , 1144.8, and 8.6 × 10¹³ Jones (fig. S18), respectively. These three parameters are also calculated using the whole device area of 3.4 mm² for comparison, as shown in Fig. 5F. Because of the low dark current and considerable photocurrent, these performance parameters of the 2% FAH FAMACs detector are among the recordhigh detectivity for perovskite photodetectors (47, 48). In addition, the 2% FAH FAMACs SC detectors also have a wider linear response range than the detectors based on 0% FAH FAMACs SC (fig. S19). The response speed that reflects the ability of a photodetector to track fast-varying optical signal was also studied. The response speed (decay) of the FAMACs photodetector was measured by the transient photocurrent (TPC) method. Figure 5G shows the TPC decay curves of the 2% FAH FAMACs SC and 0% FAH FAMACs SC devices. By fitting the TPC decay curves with the single exponential decay function, the response time of the 2% FAH FAMACs SC and 0% FAH FAMACs SC devices was derived to be 15.6 and 20.8 µs, respectively. For a photodetector, the transit time-limited -3 dB cutoff frequency can be expressed as (49)

$$f_{-3\mathrm{dB}} = \frac{0.443}{\tau_{\mathrm{tr}}}$$

where τ_{tr} is the transit time of the device, which can be estimated from the TPC time of devices. On the basis of the TPC time, the -3~dB cutoff frequencies of 2% FAH FAMACs SC and 0% FAH FAMACs SC devices are calculated to be 28.4 and 21.3 kHz. The frequency responses of the devices were studied with a square wave voltage–driven laser as the light source and an oscilloscope recording the

photocurrents of the devices under different frequencies. From the amplitude of the photocurrent, we can obtain the frequency response of the devices. As shown in Fig. 5H, the -3 dB cutoff frequencies of the 2% FAH FAMACs SC and 0% FAH FAMACs SC devices are 27.6 and 20.7 kHz, which is in accordance with that calculated from the TPC measurements. Note that the response speed is heavily dependent on device design. The present response speed is among the fastest in all perovskite photodetectors using the similar device structure



Fig. 6. Demonstration of the 2% FAH FAMACs SC integrated circuits for applications in optical imaging. (A to **C**) Schematic illustration of the measurement setup for an integrated photodetector array (12 × 12–pixel matrix) in a chip used for optical imaging. (**D** to **F**) Photocurrent responses of a 2 × 2–pixel matrix photodetector. Top: Photocurrent signals versus time, recorded by selectively illuminating the pixels of a 2 × 2 detector matrix. A 460-nm wavelength laser beam is used as the illumination source. Note that the baseline of the photocurrent signals is shifted in the *y* axis for clarity. Bottom: Illustration of the device being tested with the green box indicating the detector of the matrix under illumination. In particular, in (D), only pixels (1,1) and (1,2) are irradiated; in (E), only pixels (1,1) and (2,2) are irradiated; and in (F), only pixels (1,1) and (2,2) are irradiated. (**G**) 3D contrast maps showing the current of 12 × 12–pixel matrix photodetector array in the dark and upon 460-nm light illumination with different intensities. (**H**) Current in the dark and under light illumination for each pixel device. (**I**) Photograph and corresponding 3D current mapping of a metal annular ring imaged by a single-pixel device. Scale bar, 5 mm. Photo credit: Yucheng Liu, Shaanxi Normal University.

(as compared in table S2). In addition, good stability of the 2% FAH FAMACs SC device was also demonstrated by photocurrent measurement (fig. S20).

To evaluate the imaging performance of the device, a computerized multichannel data acquisition system is needed, as illustrated in Fig. 6 (A to C). As an example, a 2×2 -pixel matrix was tested under illumination. Because of their high optoelectronic response, only low light intensity of 5.1 μ W cm⁻² was used. The photocurrent output signals from each pixel are simultaneously measured using a four-channel oscilloscope. Figure 6 (D to F) shows the dynamic photocurrent responses recorded when (D) only pixels (1,1) and (1,2) are irradiated, (E) only pixels (1,1) and (2,1) are irradiated, and (F) only pixels (1,1) and (2,2) are irradiated. The schematic and the pixels indexing used are reported at the bottom of each graph, with a green box indicating the pixels under irradiation. All four pixels respond to the radiation with the same dynamic behavior, and the irradiated pixels can be clearly identified and easily distinguished from the nonillumination ones. Moreover, the pixels exhibit the same outputs when illuminated within the same active area. For practical applications, it is crucial to verify the uniformity of photoresponse performance of all pixels with the same illumination intensity. To verify the feasibility of the self-powered photodetector array for device integration purpose, the uniformity of photo response performance of a 12×12 -pixel devices was further explored. As shown in Fig. 6G, an integrated solar module (five cells interconnected in series to assure sufficient voltage output) was designed as the power supply for the system. The dark current of the 12×12 -pixel matrix photodetector was measured to be 6 ± 2 nA (Fig. 6H). When light illumination is switched on, the current jumps up. The light current is measured to be 210 ± 3 nA when the light intensity is 7.6 μ W cm^{-2} . It increases to 418 ± 5 nA when the light intensity is increased to 16.3 μ W cm⁻². It is obvious that all of the devices exhibited a large $I_{\text{light}}/I_{\text{dark}}$ ratio of 35 and 70 even under very low light intensity of 7.6 and 16.3 μ W cm⁻², suggesting that the detected optical signal can be clearly distinguished from the background signal.

The above results illustrate that the present 2% FAH FAMACs SC photodetector array has excellent uniformity and high potential for application as a visible light image sensor. To test the applicability of the device, a single pixel was used to perform laser light x-y scan of a metal annular ring (optical image inserted in Fig. 6I). To conduct the measurement, we placed a metal annular ring between the light and the photodetector array; only light penetrating the unshaded region of the annular ring can be projected on the pixel. The response photocurrent of the pixel was measured and then incorporated into a three-dimensional (3D) contrast map. As observed in Fig. 6I, the shape of the character ring can be clearly identified in the high-contrast map. Under the same condition, the TCMH FAMACs SC device presents much better resolution in contrast to the MAPbI₃ SC device (fig. S21). Given a response speed much faster than the time resolution of human eyes (~42 ms) (50), patterned FAMACs perovskite SC-based visible light image sensors are expected to have some important applications, e.g., artificial electronic eyes.

In conclusion, we have demonstrated the role of reductant (formic acid) in suppressing phase segregation by reducing the oxidized iodide ions and inhibiting cation deprotonation during growth of very large TCMH FAMACs perovskite SCs. Our strategy based on formic acid enabled us to obtain state-of-the-art perovskite SCs with long carrier lifetime of 8.74 \pm 0.62 µs, high charge mobility of 219 \pm 18 cm² V⁻¹ s⁻¹, long carrier diffusion distance of 71 \pm 5 µm,

Liu *et al., Sci. Adv.* 2021; **7** : eabc8844 10 February 2021

and superior uniformity and long-term stability in ambient conditions. Furthermore, these brilliant optoelectronic properties can be successfully transferred into a high-performance SP-IC photodetector. The device exhibits large responsivity (598.6 A W⁻¹), high photoconductive gain (1613.8), excellent detectivity as high as 6.7×10^{14} cm Hz^{1/2} W⁻¹, and a fast response speed as quick as 0.88 µs in SP-IC photodetection. A conformable imaging system based on a 12 × 12 pixelated matrixes of self-powered single-crystal photodetectors was realized and tested. A good discrimination between pixels when selectively illuminated was achieved for the device relevant to imaging applications. This system opens a better avenue to SP-ICs, sensors, etc.

MATERIALS AND METHODS

Chemicals and reagents

Formamidine acetate (CH₄N₂·C₂H₄O₂; 99%), methylamine (CH₃NH₂; 40% in ethanol), hydroiodic acid (HI; 57% in water, with 1.5% H₃PO₂), hydrobromic acid (HBr; 48% in water), formic acid (HCOOH or FAH; 99%), and GBL (99%) were purchased from Aladdin Reagent Ltd. PbI₂ (99.99%), PbBr (99.99%), and CsBr (99.99%) were purchased from Xi'an Polymer Light Technology. Anhydrous ethanol and anhydrous diethyl ether were purchased from Sinopharm Chemical Reagent Ltd. Fullerene (C₆₀) and 2,9-dimethyl-4,7-diphenyl-1, 10-phenanthroline (BCP) were purchased from Sigma-Aldrich. All salts and solvents were used as received without further purification.

Materials synthesis

CH₃NH₃Br (MABr) was synthesized according to the previously reported method by reacting CH₃NH₂ and HBr with the molar ratio of 1.2:1 (51). Specifically, CH₃NH₂ and HBr react in a round-bottom flask under nitrogen atmosphere in an iced bath and with continuous stirring for 6 hours. During the reaction, the HBr solution should be added dropwise into the CH₃NH₂. After reaction, we collected the powder product by evaporating the solvent of the resulting solution using a rotary evaporator. The MABr powder was obtained after the collected powder product was dissolved in anhydrous ethanol, recrystallized using anhydrous diethyl ether three times, and then dried in a vacuum oven at 60°C for 12 hours. NH2CH=NH2I (FAI) was synthesized by reacting HI and CH₄N₂·C₂H₄O₂ in a round-bottom flask (4). The reaction was finished in ice bath and under a nitrogen atmosphere with stirring for 6 hours. Yellow-white powder was obtained by reduced pressure evaporating the solutions at 65°C for 3 hours. The products were then dissolved in anhydrous ethanol, recrystallized using anhydrous diethyl ether, and finally dried at 65°C in a vacuum oven for 24 hours.

Material property characterizations

Powder XRD patterns were collected using an x-ray diffractometer equipped (2700BH) with a Cu tube ($\lambda = 1.5406$ Å) operated at 40 kV and 30 mA. High-resolution XRD measurement was taken using X'Pert Pro MRD, with Cu K α 1 line ($\lambda = 1.5406$ Å) with V = 40 kV and I = 20 mA. Thermogravimetric analysis was performed on TA SDT-Q600 V20.9 (Build 20). UV-vis-NIR absorbance spectra of FAMACs SCs were measured at room temperature using a PerkinElmer LAMBDA 950 UV-vis-NIR spectrophotometer with an integrating sphere attachment operating in the 300- to 920-nm region. The photographs in this manuscript were taken by using an 8-megapixel digital camera. PYSA measurements were carried out on FAMACs SCs

using a Riken Keiki photoelectron spectrometer (model AC-2). The power number was set to 0.33. The collected energy range was 4.2 to 6.2 eV. UV intensity was set at 80 nW. XPS was performed on a photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific) to study the elemental composition of the FAMACs SCs. The steadystate and time-resolved PL measurements of FAMACs SCs were performed using a PicoQuant FluoTime 300 and FluoTime 100 spectrometer, with 510-nm excitation wavelength.

Growth of FAMACs SCs

FAMACs SCs were grown using inverse temperature crystallization. Specifically, a stoichiometric molar ratio of FAMACs was dissolved in GBL to prepare 1.2 M single-crystal growth solution in a glass beaker. The beaker was then sealed with plastic wrap to exclude dust, particulates, and other contaminants from the environment. Upon constant stirring at room temperature for 24 hours, the salts were completely reacted to produce a clear FAMACs precursor solution. Before use, 2% (in volume) FAH was added to the solution and stirred for 10 min to disperse; then, the solution was filtered into a clear crystal dish using Poly Tetra Fluoro Ethylene (PTFE) filter with 0.8-µm pore size. For comparison, the same solution was filtered into another clear crystal dish but without the addition of FAH. To grow the SCs of FAMACs, we transfer the crystal dish (sealed with plastic wrap) to a closed oven without vibration. The temperature of the oven was heated to 60°C, and this temperature was maintained for 5 hours. After heating the solutions at 60°C for 5 hours, the solutions were slowly heated from 60°C with a slow ramp rate of 5° C h⁻¹. When the temperature was heated to 90°C, about one to three small FAMACs crystals appeared at the bottom of the crystal dish. However, under similar conditions, the solution without FAH did not yield any crystals at 90°C. To further increase the crystal size, the temperature was gradually increased up to 110°C. The existing crystal grew larger without formation of new crystallites. For the inch-sized SCs, the large SCs were used as the seeds and continue to grow in fresh solution for two to three periods. Note that the crystallization takes about 27 days in a closed oven maintained at a regulated temperature without interruption. For the solution without FAH, much smaller crystals were obtained. These crystals were surrounded by a lot of needle-like yellow crystals. All procedures were carried out under ambient conditions and humidity of 55 to 57%.

Fabrication of integrated lateral structure perovskite FAMACs SC solar cell array

The lateral structure solar cell array was designed and fabricated on the 2% FAH FAMACs SC. First, a 20-nm-thick fullerene (C₆₀) with width of 100 µm and length of 3 mm was thermally evaporated on the top surface of a crystal, with the shape and dimension defined by a shadow mask (shown in fig. S14A, right). Subsequently, about 8-nm-thick BCP with the same shape was deposited on C₆₀. Then, half part of the C₆₀ and BCP area was covered by an integrated shadow mask with a width of 50 µm and length of 3 mm, and 150-nm-thick Au was thermal-deposited on the top surface as the electrodes. Therefore, the device structure is Au/FAMACs SC/ C₆₀/BCP/Au, and the area between the two electrodes is the final device working area of 0.15 mm². For the solar cell array, each two adjacent solar cells were connected by a Au wire with a width of 50 µm and a length of 1 mm. The photograph and schematic illustration of the integrated FAMACs SC solar cell array are shown in Fig. 5 (A and B).

Fabrication of perovskite FAMACs SC SP-IC photodetectors

The SP-IC photodetectors were made by combining the lateral structure FAMACs SC solar cell array and the lateral structure FAMACs SC photodetector array, as illustrated in Fig. 5A. The lateral structure FAMACs SC photodetector array was fabricated by depositing interdigital Au electrodes via vacuum evaporation on the same FAMACs SC. As in the photograph in Fig. 5 (A and B), the detector is integrated using 12 interdigit grid Au wires. The dimension of active channel between two adjacent Au pads is 1.7 mm in length and 2 mm in width. The grid line is 60 μ m in width and 300 nm in thickness, and the gap between two grid lines is 40 μ m. Therefore, the active area and total area of the device are about 1.36 and 3.4 mm², respectively. The lateral structure FAMACs SC solar cell array was fabricated on the same FAMACs SC as the photodetector array.

Fabrication of the devices for relative dielectric constant (ϵ) and SCLC measurements

The devices for relative dielectric constant measurements were fabricated by depositing Au electrodes (100 nm in thickness) on two opposite surfaces of the FAMACs SCs. For SCLC measurements, the devices were fabricated by depositing Au electrodes (100 nm in thickness) on two opposite surfaces of the FAMACs SCs to form the structure of Au/FAMACs SC/Au for hole-only devices. For the electron-only devices, 100-nm-thick Ag electrodes were deposited on the PCBM layer to form the Ag/PCBM/FAMACs SC/PCBM/Ag structure. PCBM was made on two opposite surfaces of the FAMACs SCs by drop coating.

Fabrication of devices for mobility measurements by time-of-flight method

An Au (25 nm) anode was deposited on the top surface of the FAMACs SC by thermal evaporation; a mask was used to define the area. Electron-transporting layers were then made at the bottom surface by depositing 20-nm C_{60} and 8-nm BCP. Last, a 25-nm Au semitransparent cathode was deposited using a thermal evaporation system through a shadow mask under high vacuum.

FAMACs single-crystal SP-IC photodetector performance measurements

All device performance characterizations were done in a dark metal box to avoid electromagnetic and ambient light disturbance. The photoresponse of the devices was measured using a Keysight B2902A source meter and a manual probe station. To measure the response speed, a 460-nm semiconductor laser driven by a signal generator (Tektronix, AFG3252C) was used as the light source to generate pulsed laser beam, and the temporal response of the device was recorded using a low-noise current preamplifier (SR570) with a mixed domain oscilloscope (Tektronix, MDO3104). Noise current at different frequencies was measured using a spectrum analyzer (Keysight 35670A) with a low-noise current preamplifier (SR570). To measure the frequency response of the devices, a 460-nm semiconductor laser driven by a signal generator (Tektronix, AFG3252C) was used as light source, and the TPCs of the devices were collected by an oscilloscope. The incident intensity was measured using an optical power meter (VEGA OPHIR PD300-UV) and calibrated with a silicon photodetector. All measurements were taken at room temperature.

Imaging measurement

The imaging capability of the self-powered integrated FAMACs SC photodetector array was measured by moving the objects on a homebuilt

x-y scanning system that can collect the current signal of the detector matched with the object positions. Specifically, the object was fixed on an x-y scanning stage between the light and the photodetector array and was allowed to move in and out of the laser beam in both the x and y directions to obtain a complete image. A Keysight B2902A source meter connected to the x-y scanning system was used to record the response current corresponding position coordinates.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/ content/full/7/7/eabc8844/DC1

REFERENCES AND NOTES

- C. C. Stoumpos, C. D. Malliakas, J. A. Peters, Z. Liu, M. Sebastian, J. Im, T. C. Chasapis, A. C. Wibowo, D. Y. Chung, A. J. Freeman, B. W. Wessels, M. G. Kanatzidis, Crystal growth of the perovskite semiconductor CsPbBr₃: A new material for high-energy radiation detection. *Cryst. Growth Des.* **13**, 2722–2727 (2013).
- C. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis, Semiconducting tin and lead iodide perovskites with organic cations: Phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorg. Chem.* 52, 9019–9038 (2013).
- Y. Liu, Z. Yang, D. Cui, X. Ren, J. Sun, X. Liu, J. Zhang, Q. Wei, H. Fan, F. Yu, X. Zhang, C. Zhao, S. F. Liu, Two-inch-sized perovskite CH₃NH₃PbX₃ (X = Cl, Br, I) crystals: Growth and characterization. *Adv. Mater.* 27, 5176–5183 (2015).
- Y. Liu, J. Sun, Z. Yang, D. Yang, X. Ren, H. Xu, Z. Yang, S. F. Liu, 20-mm-large singlecrystalline formamidinium-perovskite wafer for mass production of integrated photodetectors. *Adv. Optical Mater.* 4, 1829–1837 (2016).
- Y. Liu, Y. Zhang, Z. Yang, H. Ye, J. Feng, Z. Xu, X. Zhang, R. Munir, J. Liu, P. Zuo, Q. Li, M. Hu, L. Meng, K. Wang, D. M. Smilgies, G. Zhao, H. Xu, Z. Yang, A. Amassian, J. Li, K. Zhao, S. F. Liu, Multi-inch single-crystalline perovskite membrane for high-detectivity flexible photosensors. *Nat. Commun.* 9, 5302 (2018).
- Y. Liu, X. D. Ren, J. Zhang, Z. Yang, D. Yang, F. Y. Yu, J. K. Sun, C. M. Zhao, Z. Yao, B. Wang, Q. B. Wei, F. W. Xiao, H. B. Fan, H. Deng, L. P. Deng, S. Z. Liu, 120 mm single-crystalline perovskite and wafers: Towards viable applications. *Sci. China Chem.* **60**, 1367–1376 (2017).
- Y. Liu, Y. Zhang, Z. Yang, J. Feng, Z. Xu, Q. Li, M. Hu, H. Ye, X. Zhang, M. Liu, K. Zhao, S. Liu, Low-temperature-gradient crystallization for multi-inch high-quality perovskite single crystals for record performance photodetectors. *Mater. Today* 22, 67–75 (2019).
- 8. Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, Electron-hole diffusion lengths > 175 μ m in solution-grown CH₃NH₃PbI₃ single crystals. *Science* **347**, 967–970 (2015).
- S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science* **342**, 341–344 (2013).
- G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Gratzel, S. Mhaisalkar, T. C. Sum, Long-range balanced electron- and hole-transport lengths in organic-inorganic CH₃NH₃PbI₃. *Science* **342**, 344–347 (2013).
- 11. Best Research Cell Efficiency Records, Nation Renewable Energy Laboratory (NREL); https://www.nrel.gov/pv/cell-efficiency.html [accessed 2021].
- A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* **131**, 6050–6051 (2009).
- X. Zheng, Y. Hou, C. Bao, J. Yin, F. Yuan, Z. Huang, K. Song, J. Liu, J. Troughton, N. Gasparini, C. Zhou, Y. Lin, D.-J. Xue, B. Chen, A. K. Johnston, N. Wei, M. N. Hedhili, M. Wei, A. Y. Alsalloum, P. Maity, B. Turedi, C. Yang, D. Baran, T. D. Anthopoulos, Y. Han, Z.-H. Lu, O. F. Mohammed, F. Gao, E. H. Sargent, O. M. Bakr, Managing grains and interfaces via ligand anchoring enables 22.3%-efficiency inverted perovskite solar cells. *Nat. Energy* 5, 131–140 (2020).
- Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin, J. You, Surface passivation of perovskite film for efficient solar cells. *Nat. Photonics* 13, 460–466 (2019).
- Y. Shao, Z. Xiao, C. Bi, Y. Yuan, J. Huang, Origin and elimination of photocurrent hysteresis by fullerene passivation in CH₃NH₃Pbl₃ planar heterojunction solar cells. *Nat. Commun.* 5, 5784 (2014).
- K. Domanski, B. Roose, T. Matsui, M. Saliba, S.-H. Turren-Cruz, J.-P. Correa-Baena, C. R. Carmona, G. Richardson, J. M. Foster, F. De Angelis, J. M. Ball, A. Petrozza, N. Mine, M. K. Nazeeruddin, W. Tress, M. Grätzel, U. Steiner, A. Hagfeldt, A. Abate, Migration of cations induces reversible performance losses over day/night cycling in perovskite solar cells. *Energ. Environ. Sci.* **10**, 604–613 (2017).

- S. Yang, S. Chen, E. Mosconi, Y. Fang, X. Xiao, C. Wang, Y. Zhou, Z. Yu, J. Zhao, Y. Gao, F. De Angelis, J. Huang, Stabilizing halide perovskite surfaces for solar cell operation with wide-bandgap lead oxysalts. *Science* **365**, 473–478 (2019).
- Z. Chen, Q. Dong, Y. Liu, C. Bao, Y. Fang, Y. Lin, S. Tang, Q. Wang, X. Xiao, Y. Bai, Y. Deng, J. Huang, Thin single crystal perovskite solar cells to harvest below-bandgap light absorption. *Nat. Commun.* 8, 1890 (2017).
- A. Y. Alsalloum, B. Turedi, X. Zheng, S. Mitra, A. A. Zhumekenov, K. J. Lee, P. Maity, I. Gereige, A. AlSaggaf, I. S. Roqan, O. F. Mohammed, O. M. Bakr, Low-temperature crystallization enables 21.9% efficient single-crystal MAPbl₃ inverted perovskite solar cells. ACS Energy Lett. 5, 657–662 (2020).
- Z. Ni, C. Bao, Y. Liu, Q. Jiang, W. Q. Wu, S. Chen, X. Dai, B. Chen, B. Hartweg, Z. Yu,
 Z. Holman, J. Huang, Resolving spatial and energetic distributions of trap states in metal halide perovskite solar cells. *Science* 367, 1352–1358 (2020).
- Y. Liu, Y. Zhang, Z. Yang, D. Yang, X. Ren, L. Pang, S. F. Liu, Thinness- and shape-controlled growth for ultrathin single-crystalline perovskite wafers for mass production of superior photoelectronic devices. *Adv. Mater.* 28, 9204–9209 (2016).
- H. T. Wei, Y. J. Fang, P. Mulligan, W. Chuirazzi, H. H. Fang, C. C. Wang, B. R. Ecker, Y. L. Gao, M. A. Loi, L. Cao, J. S. Huang, Sensitive x-ray detectors made of methylammonium lead tribromide perovskite single crystals. *Nat. Photonics* **10**, 333–339 (2016).
- Y. Liu, Q. Dong, Y. Fang, Y. Lin, Y. Deng, J. Huang, Fast growth of thin MAPbl₃ crystal wafers on aqueous solution surface for efficient lateral-structure perovskite solar cells. *Adv. Funct. Mater.* 29, 1807707 (2019).
- Y. Yuan, J. Huang, Ion migration in organometal trihalide perovskite and its impact on photovoltaic efficiency and stability. *Acc. Chem. Res.* 49, 286–293 (2016).
- Y. Dang, Y. Liu, Y. X. Sun, D. Yuan, X. Liu, W. Lu, G. Liu, H. Xia, X. Tao, Bulk crystal growth of hybrid perovskite material CH₃NH₃Pbl₃. *CrstEngComm* **17**, 665–670 (2015).
- M. I. Saidaminov, A. L. Abdelhady, B. Murali, E. Alarousu, V. M. Burlakov, W. Peng, I. Dursun, L. Wang, Y. He, G. Maculan, A. Goriely, T. Wu, O. F. Mohammed, O. M. Bakr, High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization. *Nat. Commun.* 6, 7586 (2015).
- Q. Han, S. H. Bae, P. Sun, Y. T. Hsieh, Y. M. Yang, Y. S. Rim, H. Zhao, Q. Chen, W. Shi, G. Li, Y. Yang, Single crystal formamidinium lead iodide (FAPbl₃): Insight into the structural, optical, and electrical properties. *Adv. Mater.* 28, 2253–2258 (2016).
- D. B. Straus, S. Guo, R. J. Cava, Kinetically stable single crystals of perovskite-phase CsPbl₃. J. Am. Chem. Soc. 141, 11435–11439 (2019).
- L.-Q. Xie, L. Chen, Z.-A. Nan, H.-X. Lin, T. Wang, D.-P. Zhan, J.-W. Yan, B.-W. Mao, Z.-Q. Tian, Understanding the cubic phase stabilization and crystallization kinetics in mixed cations and halides perovskite single crystals. *J. Am. Chem. Soc.* **139**, 3320–3323 (2017).
- Y. Huang, Y. Zhang, J. Sun, X. Wang, J. Sun, Q. Chen, C. Pan, H. Zhou, The exploration of carrier behavior in the inverted mixed perovskite single-crystal solar cells. *Adv. Mater. Interfaces* 5, 1800224 (2018).
- O. Nazarenko, S. Yakunin, V. Morad, I. Cherniukh, M. V. Kovalenko, Single crystals of caesium formamidinium lead halide perovskites: Solution growth and gamma dosimetry. NPG Asia Mater. 9, 373 (2017).
- X. Wang, Y. Wu, G. Li, Y. Li, J. Wu, X. Zhang, Q. Li, B. Wang, J. Chen, W. Lei, Fabrication of photodiodes based on solution-processed perovskite single crystals. *IEEE Trans. Electron Devices* 66, 485–490 (2019).
- Y. Fang, A. Armin, P. Meredith, J. Huang, Accurate characterization of next-generation thin-film photodetectors. *Nat. Photonics* 13, 1–4 (2018).
- M. I. Saidaminov, A. L. Abdelhady, G. Maculan, O. M. Bakr, Retrograde solubility of formamidinium and methylammonium lead halide perovskites enabling rapid single crystal growth. *Chem. Commun.* 51, 17658–17661 (2015).
- M. Saliba, T. Matsui, K. Domanski, J. Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J. P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, M. Gratzel, Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. *Science* 354, 206–209 (2016).
- D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Horantner, A. Haghighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz, H. J. Snaith, A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. *Science* 351, 151–155 (2016).
- M. I. Saidaminov, J. Kim, A. Jain, R. Quintero-Bermudez, H. Tan, G. Long, F. Tan, A. Johnston, Y. Zhao, O. Voznyy, E. H. Sargent, Suppression of atomic vacancies via incorporation of isovalent small ions to increase the stability of halide perovskite solar cells in ambient air. *Nat. Energy* **3**, 648–654 (2018).
- D. Wei, F. Ma, R. Wang, S. Dou, P. Cui, H. Huang, J. Ji, E. Jia, X. Jia, S. Sajid, A. M. Elseman, L. Chu, Y. Li, B. Jiang, J. Qiao, Y. Yuan, M. Li, Ion-migration inhibition by the cation-π interaction in perovskite materials for efficient and stable perovskite solar cells. *Adv. Mater.* **30**, e1707583 (2018).

- L. Basiricò, S. P. Senanayak, A. Ciavatti, M. Abdi-Jalebi, B. Fraboni, H. Sirringhaus, Detection of x-rays by solution-processed cesium-containing mixed triple cation perovskite thin films. *Adv. Funct. Mater.* 29, 1902346 (2019).
- L. Chen, Y.-Y. Tan, Y.-Y. Tan, Z.-X. Chen, T. Wang, S. Hu, Z.-A. Nan, L.-Q. Xie, Y. Hui, J.-X. Huang, C. Zhan, S.-H. Wang, J.-Z. Zhou, J.-W. Yan, B.-W. Mao, Z.-Q. Tian, Toward long-term stability: Single-crystal alloys of cesium-containing mixed cation and mixed halide perovskite. *J. Am. Chem. Soc.* 141, 1665–1671 (2019).
- H. X. Dang, K. Wang, M. Ghasemi, M.-C. Tang, M. De Bastiani, E. Aydin, E. Dauzon, D. Barrit, J. Peng, D.-M. Smilgies, S. De Wolf, A. Amassian, Multi-cation synergy suppresses phase segregation in mixed-halide perovskites. *Joule* 3, 1746–1764 (2019).
- Q. Lv, Z. Lian, Q. Li, J. L. Sun, Q. Yan, Formic acid: An accelerator and quality promoter for nonseeded growth of CH₃NH₃Pbl₃ single crystals. *Chem. Commun.* 54, 1049–1052 (2018).
- C. Yang, J. K. El-Demellawi, J. Yin, D. B. Velusamy, A.-H. M. Emwas, A. M. El-Zohry,
 I. Gereige, A. AlSaggaf, O. M. Bakr, H. N. Alshareef, O. F. Mohammed, MAPbl₃ single crystals free from hole-trapping centers for enhanced photodetectivity. *ACS Energy Lett.* 4, 2579–2584 (2019).
- S. S. Nepurek, Use of space-charge-limited current measurements to determine the properties of energetic distributions of bulk traps. J. Appl. Phys. 51, 2098 (1980).
- W. Wei, Y. Zhang, Q. Xu, H. Wei, Y. Fang, Q. Wang, Y. Deng, T. Li, A. Gruverman, L. Cao, J. Huang, Monolithic integration of hybrid perovskite single crystals with heterogenous substrate for highly sensitive x-ray imaging. *Nat. Photonics* **11**, 315–321 (2017).
- A. A. Zhumekenov, M. I. Saidaminov, M. A. Haque, E. Alarousu, S. P. Sarmah, B. Murali, I. Dursun, X. H. Miao, A. L. Abdelhady, T. Wu, O. F. Mohammed, O. M. Bakr, Formamidinium lead halide perovskite crystals with unprecedented long carrier dynamics and diffusion length. *ACS Energy Lett.* 1, 32–37 (2016).
- L. Dou, Y. M. Yang, J. You, Z. Hong, W. H. Chang, G. Li, Y. Yang, Solution-processed hybrid perovskite photodetectors with high detectivity. *Nat. Commun.* 5, 5404 (2014).
- M. Ahmadi, T. Wu, B. Hu, A review on organic-inorganic halide perovskite photodetectors: Device engineering and fundamental physics. *Adv. Mater.* 29, 1605242 (2017).
- C. Bao, Z. Chen, Y. Fang, H. Wei, Y. Deng, X. Xiao, L. Li, J. Huang, Low-noise and largelinear-dynamic-range photodetectors based on hybrid-perovskite thin-single-crystals. *Adv. Mater.* 29, 1703209 (2017).
- R. Nasanen, H. Ojanpaa, T. Tanskanen, J. Paallysaho, Estimation of temporal resolution of object identification in human vision. *Exp. Brain Res.* 172, 464–471 (2006).
- Y. Liu, Y. Zhang, K. Zhao, Z. Yang, J. Feng, X. Zhang, K. Wang, L. Meng, H. Ye, M. Liu,
 S. F. Liu, A 1300 mm² ultrahigh-performance digital imaging assembly using high-quality perovskite single crystals. *Adv. Mater.* **30**, e1707314 (2018).
- Y. Song, W. Bi, A. Wang, X. Liu, Y. Kang, Q. Dong, Efficient lateral-structure perovskite single crystal solar cells with high operational stability. *Nat. Commun.* 11, 274 (2020).
- J. Gao, Q. Liang, G. Li, T. Ji, Y. Liu, M. Fan, Y. Hao, S. Liu, Y. Wu, Y. Cui, Single-crystalline lead halide perovskite wafers for high performance photodetectors. *J. Mater. Chem. C* 7, 8357–8363 (2019).
- F. Ye, H. Lin, H. Wu, L. Zhu, Z. Huang, D. Ouyang, G. Niu, W. C. H. Choy, High-quality cuboid CH₃NH₃Pbl₃ single crystals for high performance x-ray and photon detectors. *Adv. Funct. Mater.* 29, 1806984 (2018).
- Z. Lian, Q. Yan, T. Gao, J. Ding, Q. Lv, C. Ning, Q. Li, J. L. Sun, Perovskite CH₃NH₃Pbl₃(Cl) single crystals: Rapid solution growth, unparalleled crystalline quality, and low trap density toward 10⁸ cm⁻³. J. Am. Chem. Soc. **138**, 9409–9412 (2016).
- H. Lu, H. Zhang, S. Yuan, J. Wang, Y. Zhan, L. Zheng, An optical dynamic study of MAPbBr₃ single crystals passivated with MAPbCl₃/l₃-MAPbBr₃ heterojunctions. *Phys. Chem. Chem. Phys.* **19**, 4516–4521 (2017).
- D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, O. M. Bakr, Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **347**, 519–522 (2015).
- Z. Yang, Y. Deng, X. Zhang, S. Wang, H. Chen, S. Yang, J. Khurgin, N. X. Fang, X. Zhang, R. Ma, High-performance single-crystalline perovskite thin-film photodetector. *Adv. Mater.* 30, 1704333 (2018).

- K. Wang, C. Wu, D. Yang, Y. Jiang, S. Priya, Quasi-two-dimensional halide perovskite single crystal photodetector. ACS Nano 12, 4919–4929 (2018).
- Y. Zhang, Y. Liu, Y. Li, Z. Yang, S. Liu, Perovskite CH₃NH₃Pb(Br_xI_{1-x})₃single crystals with controlled composition for fine-tuned bandgap towards optimized optoelectronic applications. *J. Mater. Chem. C* **4**, 9172–9178 (2016).
- L. Gao, K. Zeng, J. Guo, C. Ge, J. Du, Y. Zhao, C. Chen, H. Deng, Y. He, H. Song, G. Niu, J. Tang, Passivated single-crystalline CH₃NH₃Pbl₃ nanowire photodetector with high detectivity and polarization sensitivity. *Nano Lett.* 16, 7446–7454 (2016).
- M. I. Saidaminov, V. Adinolfi, R. Comin, A. L. Abdelhady, W. Peng, I. Dursun, M. Yuan, S. Hoogland, E. H. Sargent, O. M. Bakr, Planar-integrated single-crystalline perovskite photodetectors. *Nat. Commun.* 6, 8724 (2015).
- Y. Liu, H. Ye, Y. Zhang, K. Zhao, Z. Yang, Y. Yuan, H. Wu, G. Zhao, Z. Yang, J. Tang, Z. Xu, S. Liu, Surface-tension-controlled crystallization for high-quality 2D perovskite single crystals for ultrahigh photodetection. *Matter* 1, 465–480 (2019).
- X. Gong, M. Tong, Y. Xia, W. Cai, J. S. Moon, Y. Cao, G. Yu, C. L. Shieh, B. Nilsson, A. J. Heeger, High-detectivity polymer photodetectors with spectral response from 300 nm to 1450 nm. *Science* **325**, 1665–1667 (2009).
- H. Wei, Y. Fang, Y. Yuan, L. Shen, J. Huang, Trap engineering of CdTe nanoparticle for high gain, fast response, and low noise P3HT:CdTe nanocomposite photodetectors. *Adv. Mater.* 27, 4975–4981 (2015).
- A. Gundimeda, S. Krishna, N. Aggarwal, A. Sharma, N. D. Sharma, K. K. Maurya, S. Husale, G. Gupta, Fabrication of non-polar GaN based highly responsive and fast UV photodetector. *Appl. Phys. Lett.* **110**, 103507 (2017).
- K. K. Manga, J. Wang, M. Lin, J. Zhang, M. Nesladek, V. Nalla, W. Ji, K. P. Loh, Highperformance broadband photodetector using solution-processible PbSe-TiO₂-graphene hybrids. *Adv. Mater.* 24, 1697–1702 (2012).
- G. Konstantatos, I. Howard, A. Fischer, S. Hoogland, J. Clifford, E. Klem, L. Levina,
 E. H. Sargent, Ultrasensitive solution-cast quantum dot photodetectors. *Nature* 442, 180–183 (2006).

Acknowledgments: We would like to thank L. Etgar (The Hebrew University of Jerusalem) for insightful discussion and suggestions. Funding: This work was funded by the National Key Research and Development Program of China (2017YFA0204800/2016YFA0202403), the National Natural Science Foundation of China (91733301/61674098/61604091), the program of China Scholarship Council (CSC no. 201906870044), the Strategic Priority Research Program of Chinese Academy of Sciences (XDA17040506), the DNL Cooperation Fund CAS (DNL180311), the 111 Project (B14041), and the Changjiang Scholar and Innovative Research Team (IRT 14R33). Part of the work carried out at Northwestern University was supported by the Office of Naval Research (N00014-17-1-2231). Author contributions: S.L. and Y.L. conceived and supervised the project. Y.L. synthesized the crystals and fabricated the devices. Y.L., Y.Z., X.R., W.K., K.Z., and M.G.K. characterized the material properties. Y.L., X.Z., and J.F. fabricated and measured the single-crystal solar cells. Y.L. and Z.Y. measured the photodetector performance. Y.L., Y.Z., and Z.Y. performed the imaging measurement. M.L. carried out the high-resolution x-ray rocking curve measurements. Y.L. wrote the manuscript. S.L. and M.G.K. revised the manuscript, and all the authors reviewed the manuscript. Competing interests: Y.L., Y.Z., Z.Y., and S.L. are inventors on a patent under review related to this work filed by Shaanxi Normal University (no. CN111554814A, filed on 18 August 2020). The authors declare no other competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors

Submitted 19 May 2020 Accepted 22 December 2020 Published 10 February 2021 10.1126/sciadv.abc8844

Citation: Y. Liu, Y. Zhang, X. Zhu, Z. Yang, W. Ke, J. Feng, X. Ren, K. Zhao, M. Liu, M. G. Kanatzidis, S. Liu, Inch-sized high-quality perovskite single crystals by suppressing phase segregation for light-powered integrated circuits. *Sci. Adv.* **7**, eabc8844 (2021).