Efficient luminescent solar cells based on tailored mixed-cation perovskites

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We report on a new metal halide perovskite photovoltaic cell that exhibits both very high solar-to-electric power-conversion efficiency and intense electroluminescence. We produce the perovskite films in a single step from a solution containing a mixture of FAI, PbI₂, MABr, and PbBr₂ (where FA stands for formamidinium ions and MA stands for methylammonium cations). Using mesoporous TiO₂ and Spiro-OMeTAD as electron- and hole-specific contacts, respectively, we fabricate perovskite solar cells that achieve a maximum power-conversion efficiency of 20.8% for a PbI₂/FAI molar ratio of 1.05 in the precursor solution. Rietveld analysis of x-ray diffraction data reveals that the excess PbI₂ content incorporated into such a film is about 3 wt %. Time-resolved photoluminescence decay measurements that also point to a decrease in MAPbI₃ defect states by unreacted PbI₂, in agreement with photovoltage spectroscopy measurements.

RESULTS

Here, we report for the first time on a perovskite solar cell (PSC) using a new PbI₂-enriched composition that exhibits both very high solar-to-electric PCE and intense electroluminescence. We produce the mixed-cation mixed-halide perovskite films in a single step from a solution of FAI, PbI₂, MABr, and PbBr₂ in a mixed solvent containing dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). We vary the molar ratio for PbI₂/FAI (R_{PbI₂/FAI}) from 0.85 to 1.54 while maintaining a fixed molar ratio of 5.67 for PbI₂/PbBr₂ in the precursor solutions. By using this technique, we fabricate PSC with the structure Au/Spiro-OMeTAD/perovskite/mesoporous TiO₂/compact TiO₂/FTO. We achieve the highest PCE (20.8%) with R_{PbI₂/FAI} = 1.05, corresponding to a 3% weight excess of PbI₂ in the perovskite. The photovoltaic metrics of the device are as follows: short-circuit current density (JSC) = 24.6 mA cm⁻², open-circuit voltage (VOC) = 1.16 V, and fill factor (FF) = 0.73 (Fig. 1A). By integrating the incident photon-to-electron conversion efficiency (IPCE) spectrum over the AM 1.5 photon flux, we obtain JSC values that agree within 4% of the measured values. One of the devices was sent for certification to Newport Corporation, an accredited photovoltaic testing laboratory, confirming PCEs of 19.90% (backward scan) and 19.73% (forward scan) with a JSC of 23.2 mA cm⁻² and a VOC of 1.13 V (Fig. S1). The normalized IPCE spectrum is shown in Fig. S1 as well. The commonly observed hysteresis (13, 21) is not pronounced in our
devices, as proven by $J$-$V$ curves shown in Fig. 1C (table S1), where the voltage sweep rate was varied from 10 to 5000 mV s$^{-1}$. A cross-sectional scanning electron microscopy (SEM) image of a champion PSC is shown in Fig. 1B, visualizing a thick perovskite capping layer of around 500 nm. A histogram of 40 devices (figs. S2 and S3) indicates good performance reproducibility, with an average PCE of 19.5%. A preliminary stability investigation shows that the devices stored in the dark at room temperature are relatively stable, with a PCE drop of only 0.3% for 1 month (fig. S4 and table S2).

The photovoltaic metrics of the PSCs made by varying $R_{\text{PbI}_2/\text{FAI}}$ in the precursor solution are summarized in Fig. 2 (A to D). For $R_{\text{PbI}_2/\text{FAI}} < 1$ or $R_{\text{PbI}_2/\text{FAI}} > 1.23$, the device performance deteriorates considerably. However, in the range of $R_{\text{PbI}_2/\text{FAI}} = 1-1.16$, $J_{\text{SC}}$ and FF show a plateau, whereas $V_{\text{OC}}$ increases substantially, reaching a maximum of 1.17 V at $R_{\text{PbI}_2/\text{FAI}} = 1.16$ (1.18 V without aperture; see discussion in Materials and Methods). This is the highest $V_{\text{OC}}$ observed so far for lead iodide–based PSCs on mesoporous TiO$_2$, resulting in a PCE larger than 19%. During the rise of $V_{\text{OC}}$, $J_{\text{SC}}$ maintains a large value (more than 23 mA cm$^{-2}$) because the band gap does not alter strongly for the different perovskite compositions, as shown by the absorbance spectra in fig. S5. The FF is around 0.72, indicating that a moderate excess of PbI$_2$ does

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Fig. 1. Basic characteristics of fabricated perovskite solar cells. (A) $J$-$V$ curves for the champion solar cell under AM 1.5 G illumination, measured from $V_{\text{OC}}$ to $J_{\text{SC}}$. (B) Cross-sectional SEM image of the champion cell. (C) Hysteresis measurements of one PSC at different scanning speeds under AM 1.5 G illumination.

Fig. 2. Influence and characterization of remnant PbI$_2$ in the fabricated solar cells and films as a function of the ratio between PbI$_2$ and FAI in the precursor solution. (A to D) Photovoltaic parameters $J_{\text{SC}}$ (A), $V_{\text{OC}}$ (B), FF (C), and PCE (D) versus $R_{\text{PbI}_2/\text{FAI}}$, measured under AM 1.5 G illumination (100 mW cm$^{-2}$). (E) Fraction of remnant PbI$_2$ (left axis, orange line) and relative perovskite absorbance (right axis, blue line). (F) Mean crystallite sizes of FAPbI$_3$ (left axis, green line) and PbI$_2$ (left axis, orange line) phases determined by Rietveld refinement of thin-film XRD patterns and mean crystallite size ratio of PbI$_2$/FAI (right axis).
not retard charge collection, which is efficient in these mixed perovskites, allowing for the use of 500-nm capping layers to obtain a sharp IPCE onset and extraordinarily high photocurrents. Thus, overstoichiometric PbI$_2$ in this range does not strongly influence the composition and optical properties of the perovskite films but improves their electronic quality. This allows for simultaneously high $J_{SC}$ and $V_{OC}$ but avoids the commonly observed “tradeoff” between $V_{OC}$ and $J_{SC}$ when tuning the band gap (22, 23). In the following sections, we quantify and characterize the PbI$_2$ content remaining in the film. Subsequently, we investigate the role of PbI$_2$ in reducing nonradiative recombination.

SEM images of perovskite films deposited on a mesoporous TiO$_2$/compact TiO$_2$/FTO substrate with varied $R_{PbI_2}/FAI$ are shown in fig. S6. The film morphology changes when $R_{PbI_2}/FAI < 1$ and $R_{PbI_2}/FAI > 1.23$, indicating a modification of the perovskite morphology or the appearance of new phases. To further explore the film composition, we conducted thin-film x-ray diffraction (XRD) measurements for perovskite films deposited again on mesoporous TiO$_2$/compact TiO$_2$/FTO substrates (table S3 and figs. S7 and S8). Except for the sample with $R_{PbI_2}/FAI = 0.85$, a peak at 12.5° is observed, which is attributed to the (001) lattice planes of hexagonal (2H polytype) PbI$_2$. The PbI$_2$ content (Fig. 2E) increases with $R_{PbI_2}/FAI$, showing a 3.8% excess in weight for the most efficient device ($R_{PbI_2}/FAI = 1.05$) and a 7.5% excess in weight for the highest $V_{OC}$ device ($R_{PbI_2}/FAI = 1.16$) (table S1). These values are close to those expected from the molar ratios of the precursors in the spin-coating solution, which correspond to approximately 3 and 10 wt %, respectively. The relative amount of perovskite (Fig. 2E) deduced from absorption measurements shows a reverse trend as compared with the remnant PbI$_2$ but follows the $J_{SC}$ values (Fig. 2A), indicating that losses in $J_{SC}$ are due to reduced light harvesting rather than reduced charge collection. Because the thicknesses of all perovskite films are similar (fig. S9), the absorbance changes in absorbance indicate a significant ratio of nonperovskite material. The opposite trends in the mean crystallite sizes of PbI$_2$ and perovskite (Fig. 2F) could be due to the competitive expansion of two crystal domains. Coincidentally, the mean crystallite size of the perovskite phase follows the same trend as $V_{OC}$ (shown in Fig. 2B). The trend in the crystallite size ratio of PbI$_2$ and perovskite (Fig. 2F) mirrors that of $V_{OC}$ and reaches 0.35 for the film with the highest $V_{OC}$. Thus, excess PbI$_2$ not only exists as a crystalline phase but also influences the morphology and crystallite size of the perovskite phase. The observed correlation of the open-circuit voltage with the mean crystallite size is likely due to the fact that larger perovskite crystallites exhibit a reduced area of grain boundaries. Consequently, the overall density of defect states is lower.

**DISCUSSION**

To study the electronic quality of the device and to identify the recombination mechanisms limiting $V_{OC}$, we performed electroluminescence measurements in which we applied a forward bias to the solar cell in the dark and operated it as a light-emitting diode (LED). Figure 3A contains data for the device ($R_{PbI_2}/FAI = 1.16$), with a $V_{OC}$ of 1.18 V. The blue curve shows injection current versus voltage, where the signature of a shunt for low voltages is followed by an exponential region dominated by recombination in the device. For voltages larger than 1.2 V, limitations by the series resistance become apparent. The red curve shows the emitted photon flux, which increases exponentially with voltage. The diode ideality factor derived from the “slope” is approximately 2 for the current and 1 for the emitted photon flux, indicating that much of the recombination happens through defects [Shockley-Read-Hall (SRH)], whereas emission originates from band-to-band recombination. The external electroluminescence quantum efficiency (EQE$_{EL}$) increases linearly with injection current (fig. S10), as expected from a device with an ideality factor of 2 (24), and approaches 0.5% for currents in the range of $J_{SC}$. This value translates into a voltage loss of $kT/e \ln(1/EQE_{EL}) = 0.14$ V, confirming the measured $V_{OC} = 1.32$ V – 0.14 V = 1.18 V (where 1.32 V is the theoretical maximum $V_{OC}$ (radiative limit)), which we determined for this solar cell using its IPCE action spectrum and following the approach of Tress et al. (11).

An EQE$_{EL}$ of 0.5% is a record for solution-processed solar cells such as organics, where it is commonly <10$^{-6}$ (25), and approaches that of the best silicon solar cells (26). Even when compared to perovskite-based LEDs, our EQE$_{EL}$ is among the highest. Our solar cell LED delivers an overall electric power to light conversion efficiency of as high as 0.5% at a voltage of 1.5 V (which is still below $E_g/e$), whereas reported LEDs show the same efficiency at voltages higher than 3 to 4 V (27, 28). An LED efficiency of 3.5% has been obtained recently, but under much larger charge carrier densities [that is, not under solar cell operating conditions (2.2 V, 160 mA cm$^{-2}$, and 50-nm layer thickness)] (29). Our high EQE$_{EL}$ indicates a high-quality perovskite film and a very good charge selectivity of the contacts, accompanied by a high built-in potential and/or very balanced injection and transport of electrons and holes.

To analyze the dynamics of recombination, we performed time-correlated single photon counting (TCSPC) measurements at different excitation fluences. The photoluminescence (PL) decays for perovskite films with $R_{PbI_2}/FAI = 1$ and $R_{PbI_2}/FAI = 1.16$ deposited on mesoporous TiO$_2$/compact TiO$_2$/FTO substrate are shown in Fig. 3 (B and C) (for all samples in figs. S11 and S12).

For the highest light intensity generating approximately $n = 2 \times 10^{17}$ charges per cubic centimeter, the overall decay becomes faster as a result of direct electron-hole recombination, where the recombination coefficient $\beta \approx 2 \times 4 \times 10^{-11}$ cm$^3$ s$^{-1}$ in $dn/dt = -\beta n^2 - kn$ describes radiative recombination resulting in the expected $V_{OC}$ of $\approx 1.3$ V (derivation in Materials and Methods). For long time scales or decreased excitation intensity, the PL shows monoexponential decay characteristic of SRH recombination. We deduced 220 and 350 ns, respectively, as nonradiative lifetimes $1/k$ for the two perovskite films with $R_{PbI_2}/FAI = 1$ and $R_{PbI_2}/FAI = 1.16$, consistent with the trend in $V_{OC}$. In addition, the signal drops strongly in the first few nanoseconds as a result of trap filling. The loss of PL is more significant for the stoichiometric perovskite/TiO$_2$ interface as compared to the mixed perovskite/TiO$_2$ interface or a better quality of the perovskite crystallites.

To further elucidate this, we investigate $V_{OC}$ as a function of illumination intensity, represented by $J_{SC}$ in Fig. 3D ($J_{SC} \propto$ intensity). The dashed lines visualizing the theoretical slope for SRH recombination indicate that $V_{OC}$ is mainly limited by SRH recombination. The device with $R_{PbI_2}/FAI = 1.16$ shows a reduced slope toward higher intensities. This is consistent with the bending seen in EQE$_{EL}$ as a function of injection current (fig. S10). Because $V_{OC}$ is still below the radiative limit, this reduced slope is most likely due to losses of charges at a nonperfectly selective contact.
We use illumination with different wavelengths to tune the absorption profile in the perovskite film. Because of the strong dependence of the absorption coefficient on wavelength (fig. S5), red light (630 nm) and blue light (460 nm) penetrate the film to varied extent: 90% of the blue light is absorbed over a distance <200 nm away from FTO, whereas red light penetrates much farther. Figure 3D shows a significant difference only for the stoichiometric device, where $V_{OC}$ is lower for blue illumination despite the fact that the generated charge carrier density is higher. This is in accordance with the PL decay and proves that this device shows its highest defect density close to TiO$_2$, the impact of which is reduced in the presence of overstochiometric PbI$_2$.

From the PL decay and the monochromatic $V_{OC}$ study, we contend that the role of excess PbI$_2$ is to reduce recombination close to the perovskite/TiO$_2$ interface. Thus, PbI$_2$ crystallites, which are located within the mesoporous TiO$_2$ scaffold, prevent recombination of holes photogenerated in this region of the absorber. Furthermore, PbI$_2$ crystallites, which are present within the mesoporous TiO$_2$ layer, favor the growth of bigger perovskite crystallites, which exhibit a reduced area of grain boundaries and, therefore, fewer defects.

To conclude, we have shown that an excess of PbI$_2$ of up to ≈8 wt % can enhance the electronic quality of the perovskite/TiO$_2$ film. With the adoption of this approach, devices based on mixed perovskite enabled a PCE of 20.8% and an open-circuit voltage of 1.18 V, accompanied by a high external electroluminescence quantum efficiency of 0.5%, which is attributed to reduced recombination via defects due to a moderate excess of PbI$_2$. Further optimization along this path will lead to solution-processed solar cells approaching the theoretical limits for open-circuit voltage and efficiency.

**MATERIALS AND METHODS**

**Materials**

All materials were purchased from Sigma-Aldrich and used as received, unless stated otherwise.
**Synthesis of inorganic/organic halide materials**

NH$_2$C$\text{H}$$\text{N}$H$_3$I was synthesized by slowly dropping 15 ml of hydroiodic acid (45 wt % in water) (Applichem) to a solution of 5 g of formamide acetate in methanol cooled at 0°C. The solution was then stirred for 5 hours at room temperature. The yellow-light solution was concentrated by rotary evaporation at 80°C until no obvious liquid remained. The crude solid was then dissolved by a minimum amount of methanol, recrystallized in diethyl ether, and filtered. The procedure was performed three times, and the resulting white solid was collected and dried at 80°C under vacuum for 2 days. $^1$H nuclear magnetic resonance (DMSO-d$_6$) δ 8.76 (s, 4H), 7.85 (s, 1H) ppm; $^{13}$C nuclear magnetic resonance (DMSO-d$_6$) δ 157.05 ppm.

CH$_3$NH$_3$Br was synthesized by slowly dropping 31.1 ml of hydrobromic acid (48 wt % in water) (Fluka) to a solution of 27.86 ml of CH$_3$NH$_2$ (40 wt % solution in absolute methanol; TCI) cooled at 0°C. The solution was further stirred for 5 hours at room temperature. The colorless solution was concentrated by rotary evaporation at 50°C until no obvious liquid remained. The crude solid was then dissolved by a minimum amount of ethanol, recrystallized in diethyl ether, and filtered. The procedure was repeated three times, and the resulting white solid was collected and dried at room temperature under vacuum for 2 days.

**Solar cell preparation**

The fluorine-doped tin oxide–coated glass (NSG) was sequentially cleaned using detergent, acetone, and ethanol. A 20- to 30-nm TiO$_2$ blocking layer was deposited on the cleaned FTO by spray pyrolysis, using O$_2$ as carrier gas, at 450°C from a precursor solution of 0.6 ml of titanium diisopropoxide and 0.4 ml of bis(acetylacetonate) in 7 ml of anhydrous isopropanol. A 200-nm mesoporous TiO$_2$ was coated on the substrate by spin coating at a speed of 4500 rpm for 15 s with a ramp-up of 2000 rpm s$^{-1}$ from a diluted 30-nm particle paste (Dyesol) in ethanol; the weight ratio of TiO$_2$ (Dyesol paste) to ethanol is 5:1. After spin coating, the substrate was immediately dried on a hotplate at 80°C, and the substrates were then sintered at 500°C for 20 min. The perovskite film was deposited by spin coating onto the TiO$_2$ substrate. The precursor solution was prepared in a glovebox of 1.35 M PbI$_2$ (PbI$_2$ and PbBr$_2$) in a mixed solvent of DMF and DMSO; the volume ratio of DMF to DMSO was 4:1. The molar ratio for PbI$_2$ (specified purity >98%; TCI)/PbBr$_2$ (purity, 99.999%; Alfa Aesar) was fixed at 0.85:0.15, and the molar ratio for MABr/PbBr$_2$ was fixed at 1:1. A comprehensive analysis carried out by an analytical institution and covering more than 70 elements showed that the purity of the TCI product (PbI$_2$) exceeded 99.99%. Thus, it was much purer than specified, implying that changes in molar ratio within the range of some percentages in the precursor solutions are not superimposed by the effects of impurities.

By changing the amount of FAI, we obtained different molar ratios for PbI$_2$/FAI varying from 1.54 to 1.37, 1.23, 1.16, 1.10, 1.05, and 0.85. The spin-coating procedure was performed in an argon flowing glovebox: first, 2000 rpm for 10 s with a ramp-up of 200 rpm s$^{-1}$; second, 6000 rpm for 30 s with a ramp-up of 2000 rpm s$^{-1}$. Chlorobenzene (110 μl) was dropped on the spinning substrate during the second spin-coating step 20 s before the end of the procedure. The substrate was then heated at 100°C for 90 min on a hotplate. After cooling down to room temperature, Spiro-OMeTAD (Merck) was subsequently deposited on top of the perovskite layer by spin coating at 3000 rpm for 20 s. The Spiro-OMeTAD solution was prepared by dissolving Spiro-OMeTAD in chlorobenzene (60 mM), with the addition of 30 mM bis(trifluoromethanesulfonyl)imide (from a stock solution in acetonitrile) and 200 mM tert-butylpyridine.

Finally, FK209 [tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris((trifluoromethylsulfonyl)imide ]); Dynamo AB] was added to the Spiro-OMeTAD solution (from a stock solution in acetonitrile); the molar ratio for FK209 and Spiro-OMeTAD was 0.03. Finally, 80 nm of gold was deposited by thermal evaporation using a shadow mask to pattern the electrodes.

**Characterization**

Current-voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley model 2400). The light source was a 450-W xenon lamp (Oriel) equipped with a Schott K113 Tempax sunlight filter (Prazelisgns Glas & Optik GmbH) to match the emission spectrum of the lamp with the AM 1.5 G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cutoff filter (Schott KG-3).

To specify the illuminated area, we used an aperture (shadow mask) with an area of 0.16 cm$^2$, whereas the total device area defined by the overlap of the electrodes was approximately 0.36 cm$^2$. This approach allows for an accurate determination of the short-circuit current density but has drawbacks when determining the open-circuit voltage ($V_{OC}$) as $V_{OC}$ depends on the dark current flowing through the device according to the equation: $V_{OC} = n_0 q k T / e \ln(I_S/I_0) + 1$. If there is a mismatch between the illuminated area and the dark area, the ratio between the photocurrent $I_S$ and the dark saturation current $I_0$ is artificially changed by this ratio. Therefore, the open-circuit voltage was additionally measured without aperture.

XRD spectra were recorded on an X’Pert MPD PRO (PANalytical) equipped with a ceramic tube providing Ni-filtered (CuKα, λ = 1.54060 Å) radiation and on an RTMS X’Celerator (PANalytical). The measurements were performed in Bragg-Brentano geometry 2θ = 8° to 88°. The samples were mounted without further modification, and the automatic divergence slit (10 mm) and beam mask (10 mm) were adjusted to the dimension of the films. A step size of 0.008° was chosen for an acquisition time of 270.57 s deg$^{-1}$. A baseline correction was applied to all x-ray thin-film diffractograms to compensate for the broad feature arising from the FTO glass and anatase substrate. The presence of strong thermal diffuse scattering and turbostratic disorder, mainly in the PbI$_2$ films, thwarted a successful Rietveld refinement of up to six phases. Finally, the areas of the (001) maximum of PbI$_2$ and the (011)/(101) peaks of FAPbI$_3$ calculated by means of a pseudo-Voigt function, were used to estimate the weight fractions. These pseudo-Voigt functions also furnished the full widths at half maximum, which were subsequently used to compute the sizes of the coherent domains along the diffraction vectors by means of Scherrer’s equation, setting $K = 1$. SEM images were recorded using a high-resolution scanning electron microscope (Zeiss Merlin).

**Electroluminescence yield.** The emitted photon flux was detected with a large-area (1 cm$^2$) Si-photodiode (Hamamatsu S1227-1010BQ) positioned close to the sample. Because of the nonconsidered angular dependence of emission and detector sensitivity, EQE$_{EL}$ was expected to be slightly underestimated (on the order of 10%). The driving voltage was applied using a Bio-Logic SP300 potentiostat, which was also used to measure the short-circuit current of the detector at a second channel.
Absorption spectra were measured on a PerkinElmer ultraviolet (UV)–vis spectrophotometer. Absorbance was determined from a transmittance measurement using an integrating sphere. We used the “PerkinElmer Lambda 950 nm” setup with the integrating sphere system “60 nm InGaAs integrating sphere.” The sources were deuterium and tungsten halogen lamps, and the signal was detected by a gridless photomultiplier with Peltier-controlled PbS detector. The UV WinLab software was used to process the data.

**PL and TCSCP experiments.** PL spectra were recorded by exciting the perovskite films deposited onto mesoporous TiO₂ at 460 nm with a standard 450-W Xenon CW lamp. The signal was recorded with a spectrophotometer (Fluorometer; Horiba Jobin Yvon Technology FL1065) and analyzed with the software FluorEssence.

The PL decay experiments were performed on the same samples using the same Fluorometer with a pulsed source at 406 nm (Horiba NanoLED 402-LH; pulse width <200 ps, 11 pJ per pulse, approximately 1 mm² in spot size), and the signal was recorded using TCSCP. The samples were excited from the perovskite and glass side under ambient conditions.

**Analysis of the PL decay.** From the pump fluence, we estimated an initial photogenerated charge carrier density on the order of $2 \times 10^{17}$ cm⁻³ upon excitation at the highest intensity. For a filter with a transmittance of 2.5%, we expected $5 \times 10^{15}$ cm⁻³. Assuming that most of the charge carriers in the perovskite are photogenerated (that is, the intrinsic charge carrier density is low), we can set the electron density equal to the hole density and write the continuity equation for photogenerated electrons: $dn/dt = -n \beta \gamma^2 - kn$, assuming that changes in the charge density $n$ are due to either a bimolecular process or monomolecular recombination. Solving this equation for $n(t)$ and assuming that the PL signal is proportional to $n'(t)$, we can calculate the PL decay (solid lines in the main paper).

The ideal solar cell without nonradiative recombination should have $k = 0$. Then, $V_{OC}$ can be calculated, assuming that the charge carrier generation rate $G$ equals the recombination rate $R$: $G = R = \beta \gamma^2$. For a semiconductor using Boltzmann statistics and effective mass approximation, $V_{OC}$ can be written as $V_{OC} = E_g - kT \ln(N_eN_h/np)$, with the effective densities of states in conduction and valence bands: $N_{CV} = 2 \times (2\pi\hbar^2)k^2T/h^3/2$. Thus, knowing the effective mass $m_{eff}$, temperature $T$, band gap $E_g$, and light intensity, $V_{OC}$ can be calculated as $V_{OC} = E_g e^{-kT e \ln(N_eN_h/np)} \approx 1.3$ V, where we approximated $G = \beta \gamma^2(e \times$ thickness $) = 3 \times 10^{27}$ m⁻³ s⁻¹. This is a rough estimation where the order of magnitude of the input parameters—but not their exact values—is known. Effective masses have been taken from Giorgi et al. (30).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/1/e1501170/DC1

**REFERENCES AND NOTES**


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