Supporting Information

Highly Reproducible and Efficient FASnI$_3$

Perovskite Solar Cells Fabricated with

Volatilizable Reducing Solvent

Xiangyue Meng$^{1,2,\#}$, Tianhao Wu$^{1,\#}$, Xiao Liu$^2$, Xin He$^2$, Takeshi Noda$^2$, Yanbo Wang$^1$, Hiroshi Segawa$^3$ and Liyuan Han$^{1,2,4,*}$

$^1$State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, China

$^2$Photovoltaic Materials Group, Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan

$^3$Research Center for Advanced Science and Technology, University of Tokyo, Tokyo 153-8904, Japan

$^4$School of Materials Science and Engineering, Henan Institute of Advanced Technology, Zhengzhou University, Zhengzhou 450001, China

AUTHOR INFORMATION

Corresponding Author
* Han.liyuan@sjtu.edu.cn

Author Contributions

# X.M. and T.W. contributed equally to this work.
Materials and Methods

Materials. All chemicals were used as received without further purification, including FAI (> 98%, Tokyo Chemical Industry Co., Japan), SnI₂ beads (99.99%, Sigma-Aldrich), SnF₂ (>99%, Sigma-Aldrich), poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT:PSS) (Clevios P VP Al 4083), fullerene-C₆₀ sublimed (99.9%, Sigma-Aldrich), oxalic acid (99.999% trace metals basis, Sigma-Aldrich). Bathocuproine (BCP) and super dehydrated solvents of dimethyl sulfoxide (DMSO), chlorobenzene, and formic acid (99.5%, for high performance liquid chromatography) were purchased from Wako Co., Japan.

Perovskite film fabrication. The precursor solution for the FASnI₃-50%LFA perovskite film was prepared by mixing SnI₂ (1 mmol), FAI (1 mmol), 10% SnF₂ (0.1 mmol) and 50 mol% of LFA (0.5 mmol, 19 μL) in 981 μL of DMSO solvent. The perovskite precursor solution was then spin-coated at 1000 rpm for 12 s and then 5000 rpm for 60 s; chlorobenzene (135 μL) was dripped onto the perovskite film at 40 s after the rotation speed was increased to 5000 rpm. The resulting films were annealed at 60 °C for 10 s and then at 100 °C for 14 min. Deposition of the perovskite film was done under a flow of nitrogen gas in a glovebox to avoid the accumulation of solvent inside of spin-coater.

Solar cell fabrication. Perovskite solar cells (PSCs) were fabricated on patterned indium tin oxide (ITO) coated glass substrates. The substrates were ultrasonically cleaned with detergent, de-ionized water, acetone, and ethanol, respectively, for 15 min each. The cleaned substrates were treated with ultraviolet ozone for 30 min. The hole transport layer was deposited on top of the ITO substrate by spin-coating 100 μL of PEDOT:PSS solution at 4000 rpm for 30 s. The PEDOT:PSS films were then annealed at 160°C for 15 min. Then the substrates were transferred to a glove box and the perovskite films were deposited. Then 35 nm of fullerene C₆₀ and 8 nm of BCP were sequentially evaporated on the perovskite layer. Finally, a 70 nm thick silver layer was vacuum deposited with device area of 0.35 cm × 0.35 cm. The PSCs were sealed by a cavity glass using UV curable glue (ThreeBond) on top of the front active
area of ITO. After exposure to 300 W UV light for 15 seconds, the sealing process was
terminated. All of these processes were done in nitrogen filled glove box.

**Characterization.** UV-Vis absorption spectra were obtained using a UV-Vis-NIR
spectrophotometer (7200, V-JASCO). Photoluminescence and time-resolved
photoluminescence decay were measured with a Hamamatsu fluorescence spectrometer. The
morphology of the films and structures of the devices were observed by scanning electron
microscope (JSM-6500F field-emission under an acceleration voltage of 5 kV). The X-ray
diffraction (XRD) patterns were measured with an X-ray diffractometer (Rigaku SmartLab,
Japan, Cu Kα, λ = 1.54050 Å). The current-voltage (J-V) curves were measured by using a
solar simulator with standard air mass 1.5 sunlight (100 mW/cm², WXS-155S-10, Wacom
Denso Co., Japan), and the J-V curves were measured under forward scan (-0.1 V to 0.7 V) or
reverse scan (0.7 V to -0.1 V) in air after light soaking for several hours, the step voltage was
fixed at 10 mV and the delay time was set at 50 ms. The solar cells were measured using a
black shadow mask with the aperture area of 0.09 cm². The reference cell was calibrated by
the Calibration, Standards and Measurement Team at the Research Center for Photovoltaics in
the National Institute of Advanced Industrial Science and Technology, Japan. The spectral
mismatch was less than 3%. Monochromatic IPCE spectra were measured with
monochromatic incident light (1 × 10¹⁶ photons/cm²) in direct current mode (CEP-2000BX,
Bunkoukeiki Co., Ltd). The operational stability was tested on a solar cell light resistance test
system (Model BIR-50, Bunkokeiki) with a Class AAA solar simulator. The
capacitance-frequency (C-f) spectrum was measured by using an LCR meter (E4980A,
Agilent), which probed from 20 Hz to 2 MHz at an AC voltage amplitude of 30 mV in the
dark at room temperature. The capacitance-voltage (C-V) measurements were taken at 100 Hz
with a voltage amplitude of 30 mV in the dark at room temperature. Note that the scan
frequency was determined from the plateau region (corresponds to geometrical capacitance)
of the $C-f$ scan at zero bias. For SCLC measurement, the dielectric constant of FASnI$_3$ is estimated at 25.

**Figure S1.** Scanning electron microscope images of (a) the pristine FASnI$_3$ perovskite film and the FASnI$_3$ perovskite films with (b) 2 mol% solid oxalic acid (SOA), (c) 5 mol% SOA, (d) 10 mol% SOA.

**Figure S2.** X-ray diffraction patterns of the FASnI$_3$ perovskite films with different amounts of solid oxalic acid (SOA).
Figure S3. (a) Proton nuclear magnetic resonance spectra of the FASnI$_3$-10% solid oxalic acid (SOA) perovskite film dissolved in deuterated dimethyl sulfoxide (DMSO) solution. (b) Proton nuclear magnetic resonance spectra of solid oxalic acid (SOA) with or without addition of SnI$_2$ in deuterated dimethyl sulfoxide (DMSO) solution.
Figure S4. Time-resolved photoluminescence decay spectra of the FASnI$_3$ perovskite films with different amounts of solid oxalic acid (SOA).

Figure S5. Reverse scanning $J$-$V$ curves of the best devices based on FASnI$_3$ with different amounts of liquid formic acid (LFA).
Figure S6. Cross section scanning electron microscope images of the FASnI$_3$ perovskite films with different amounts of liquid formic acid (LFA), (a) 20 mol% LFA, (b) 50 mol% LFA and (c) 100 mol% LFA.

Figure S7. Absorption spectra of the FASnI$_3$ perovskite films with different amounts of liquid formic acid (LFA).
**Figure S8.** $J$-$V$ curves of the best devices based on FASnI$_3$ with different amounts of solid oxalic acid (SOA) under the reverse scan.

**Figure S9.** Encapsulated device stability under maximum power point tracking and continuous AM1.5G one sun illumination (with a 420 nm cutoff UV filter) at 25 °C in air.
Figure S10. The distributions of open circuit voltage, current density, fill factor and power conversion efficiency of the perovskite solar cell devices under the reverse scan.

Figure S11. Admittance spectra of the solar cell devices.
Figure S12. $J$-$V$ curves of the champion perovskite solar cell devices under the reverse scan (R) and the forward scan (F).

Figure S13. Stabilized current density and power output measured at 0.50 V for the champion device with 50 mol% liquid formic acid (LFA).
Figure S14. Photoluminescence spectra of the FASnI$_3$ perovskite films with different amounts of liquid formic acid (LFA).

Figure S15. Time-resolved photoluminescence decay spectra of the FASnI$_3$ perovskite films with different amounts of liquid formic acid (LFA).
Table S1 Photovoltaic parameters of the best perovskite solar cell devices based on FASnI$_3$ with different amounts of liquid formic acid (LFA).

<table>
<thead>
<tr>
<th>Device</th>
<th>Forward</th>
<th>Reverse</th>
<th>Forward</th>
<th>Reverse</th>
<th>Forward</th>
<th>Reverse</th>
<th>Forward</th>
<th>Reverse</th>
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<tr>
<td></td>
<td>$V_{oc}$ [V]</td>
<td>$J_{sc}$ [mA cm$^2$]</td>
<td>FF</td>
<td>PCE [%]</td>
<td>$V_{oc}$ [V]</td>
<td>$J_{sc}$ [mA cm$^2$]</td>
<td>FF</td>
<td>PCE [%]</td>
</tr>
<tr>
<td>FASnI$_3$</td>
<td>0.537</td>
<td>18.10</td>
<td>0.649</td>
<td>6.31</td>
<td>0.553</td>
<td>18.10</td>
<td>0.647</td>
<td>6.48</td>
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<tr>
<td>FASnI$_3$-20%LFA</td>
<td>0.578</td>
<td>20.42</td>
<td>0.694</td>
<td>8.19</td>
<td>0.586</td>
<td>20.56</td>
<td>0.712</td>
<td>8.58</td>
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<td>FASnI$_3$-50%LFA</td>
<td>0.616</td>
<td>22.08</td>
<td>0.728</td>
<td>9.90</td>
<td>0.628</td>
<td>22.25</td>
<td>0.742</td>
<td>10.37</td>
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<td>FASnI$_3$-100%LFA</td>
<td>0.602</td>
<td>20.12</td>
<td>0.711</td>
<td>8.61</td>
<td>0.611</td>
<td>20.26</td>
<td>0.728</td>
<td>9.01</td>
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Table S2 Photovoltaic parameters of the best perovskite solar cell devices based on FASnI$_3$ with different amounts of solid oxalic acid (SOA).

<table>
<thead>
<tr>
<th>Device</th>
<th>Forward</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FASnI$_3$</td>
<td>0.537</td>
<td>18.10</td>
<td>0.649</td>
<td>6.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.553</td>
<td>18.10</td>
<td>0.647</td>
<td>6.48</td>
<td></td>
</tr>
<tr>
<td>FASnI$_3$-2%SOA</td>
<td>0.515</td>
<td>17.361</td>
<td>0.682</td>
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<tr>
<td></td>
<td>0.534</td>
<td>17.556</td>
<td>0.694</td>
<td>6.50</td>
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<td>FASnI$_3$-5%SOA</td>
<td>0.412</td>
<td>15.750</td>
<td>0.622</td>
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<td></td>
<td>0.428</td>
<td>15.896</td>
<td>0.634</td>
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<td>FASnI$_3$-10%SOA</td>
<td>0.325</td>
<td>10.778</td>
<td>0.453</td>
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<td></td>
<td>0.342</td>
<td>10.750</td>
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**Table S3** Photovoltaic parameters of the perovskite solar cell devices based on FASnI$_3$ with different concentration of the perovskite precursor solution under the reverse scan.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF</th>
<th>PCE [%]</th>
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<tbody>
<tr>
<td>0.9 M</td>
<td>0.524</td>
<td>17.45</td>
<td>0.632</td>
<td>5.78</td>
</tr>
<tr>
<td>1 M</td>
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<td>6.48</td>
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<tr>
<td>1.1 M</td>
<td>0.517</td>
<td>20.36</td>
<td>0.598</td>
<td>6.29</td>
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### Table S4

The pH value of the perovskite precursor solution with different amount of liquid formic acid (LFA).

<table>
<thead>
<tr>
<th></th>
<th>No</th>
<th>20 mol%</th>
<th>50 mol%</th>
<th>100 mol%</th>
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<tr>
<td>pH</td>
<td>7.84</td>
<td>7.38</td>
<td>6.97</td>
<td>6.54</td>
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