Enhancement in the efficiency of an organic–inorganic hybrid solar cell with a doped P3HT hole-transporting layer on a void-free perovskite active layer

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1. Materials

**Preparation for perovskite precursor**

The perovskite precursor was prepared the following procedure in the reference.[1] Thus, 12 ml of hydroiodic acid (57 wt% in water, Sigma-Aldrich) was added dropwise in 2 h to 24 ml of methylamine (33 wt% in ethanol, Sigma-Aldrich) in 100-ml ethanol. Solvent was removed on a rotary evaporator, and the product was recrystallized from diethyl ether to obtain methylammonium iodide (MAI) as a crystalline powder. The powder was dried in a vacuum chamber at 65 °C for 12 h. In a grove box (N₂ atmosphere), MAI and PbCl₂ (Aldrich, 99.999%) were dissolved in dimethylformamide (Tokyo Chemical Industry Co., 99.5%) with a molar ratio of 3:1 and stirred for 12 h at 65 °C to obtain a precursor solution. Total material concentration was 20 wt%.

**Preparation of TiOₓ precursor**[2]

To prepare a TiOₓ precursor solution, 438 µl of commercially available titanium isopropoxide (Tokyo Chemical Industry Co.) was diluted in isopropanol 3 ml. In a separated flask, 83 µl of a 1 M HCl solution was diluted with isopropanol (3 ml), and was added dropwise to the titanium precursor solution under rapidly stirring. The solution was filtered through a PTFE membrane filter with 0.2 µm pore size just before use.

**Materials for the hole-transporting layer**

High purity regioregular P3HT (99.995%) with Mn=30000~60000, Li–TFSI (>99.0%) and D-TBP (97%) were purchased from Aldrich. High purity chlorobenzene was used as solvent for P3HT.

2. Scanning electron microscopy

SEM observations were conducted on an FEI Magellan 400L equipped with AMETEK/EDAX Genesis APEX4 at a landing voltage of 1 kV under a reduced pressure of 5 × 10⁻⁵ Pa.

![SEM image of TiOₓ coated on ITO substrate](image)

*Figure S1.* SEM image of TiOₓ coated on ITO substrate (a), and enlarge image (b)
Figure S2. Original SEM images (a,c) and void-labeled SEM images (b, d) of the rapidly cooled perovskite layer. Estimated coverage is 99.84% based on the integration of the red area in (b), and 99.71% estimated from (d). (e) Statistical analysis the coverage based on 9 different samples. The average value is 99.55% (± 0.24%).
**Figure S3.** Original SEM images (left) and void-labeled SEM images (right) of the rapidly cooled perovskite layer of slowly cooled perovskite layer. Estimated coverage is here 82.2%.

3. Photovoltaic performances

**Table S1.** The details of photovoltaic performance of solar cell using HTLs H-1 to H-6 containing P3HT, Li–TFSI and D-TBP in a variety of ratios.

<table>
<thead>
<tr>
<th>HTL</th>
<th>P3HT&lt;sup&gt;a&lt;/sup&gt; (mg)</th>
<th>Li–TFSI&lt;sup&gt;b&lt;/sup&gt; (mg)</th>
<th>D-TBP&lt;sup&gt;c&lt;/sup&gt; (mg)</th>
<th>(J_{sc}) (mA·cm&lt;sup&gt;–2&lt;/sup&gt;)</th>
<th>(V_{oc}) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>(R_s) (Ω·cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>(\sigma) (S·m&lt;sup&gt;–1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>17.7</td>
<td>0.92</td>
<td>56.2</td>
<td>9.2</td>
<td>12.4</td>
<td>5.4 × 10&lt;sup&gt;–4&lt;/sup&gt;</td>
</tr>
<tr>
<td>H-2</td>
<td>15</td>
<td>0.54</td>
<td>0</td>
<td>19.3</td>
<td>0.94</td>
<td>61.5</td>
<td>11.2</td>
<td>8.9</td>
<td>5.4 × 10&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>H-3</td>
<td>15</td>
<td>0.54</td>
<td>8.8</td>
<td>19.1</td>
<td>0.98</td>
<td>66.3</td>
<td>12.4</td>
<td>8.5</td>
<td>6.4 × 10&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>H-4</td>
<td>15</td>
<td>0</td>
<td>8.8</td>
<td>17.5</td>
<td>0.89</td>
<td>41.6</td>
<td>6.5</td>
<td>48.3</td>
<td>3.4 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>H-5</td>
<td>15</td>
<td>0.07</td>
<td>2.9</td>
<td>18.8</td>
<td>0.94</td>
<td>57.8</td>
<td>10.2</td>
<td>12.5</td>
<td>4.3 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>H-6</td>
<td>15</td>
<td>0.19</td>
<td>2.9</td>
<td>19.9</td>
<td>0.96</td>
<td>61.2</td>
<td>11.7</td>
<td>11.3</td>
<td>5.0 × 10&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>P3HT dissolved in 1 ml chlorobenzene, <sup>b</sup>Li–TFSI dissolved in 6.8 µl acetonitrile, <sup>c</sup>D-TBP (3.4 µl (2.9 mg) or 10.2 µl (8.8 mg)) was added into the P3HT:Li–TFSI mixture solution.
Figure S4. J-V curves of the cell using H-2, H-4, H-5, and H-6 as HTL.

Figure S5. J-V curves and the photovoltaic parameters of the cell using D-TBP or TBP (3.4 μl) added P3HT (15 mg dissolved in 1 ml chlorobenzene) with the Li-TFSI (6.8 μl acetonitrile).

<table>
<thead>
<tr>
<th>Additive</th>
<th>J_{sc} (mA·cm^{-2})</th>
<th>V_{oc} (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-TBP</td>
<td>17.7</td>
<td>0.91</td>
<td>59.0</td>
<td>9.1</td>
</tr>
<tr>
<td>TBP</td>
<td>17.6</td>
<td>0.94</td>
<td>54.0</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Figure S6. Solar cell performances of the H-3 devices. (a) Statistical distribution of 23 devices. The average value of PCE is 11.1% (± 0.55%). (b) Photocurrent density and power conversion efficiency at 0.7 V applying voltage under the irradiation of 10.8% device.
4. Absorption and photoluminescence spectra

Absorption spectrum of the perovskite thin films was recorded on a Jasco V-670 spectrophotometer, and photoluminescence was examined on a fluorescence spectrophotometer (HITACHI, F-4500).

![Absorption and Photoluminescence Spectra](image)

**Figure S7.** Absorption spectrum of the perovskite thin films (a), and the photoluminescence (b) from the perovskite on the different configuration perovskite/pristine P3HT, TiO$_x$/perovskite and TiO$_x$/perovskite/pristine P3HT. All thin films were coated on to the quartz substrate.

5. Transporting property and X-ray diffraction

To measure the field-effect mobility, we fabricated bottom-gate/bottom contact field-effect transistor devices on SiO$_x$/Si wafer. Highly doped Si and SiO$_x$ (300 nm) formed gate electrode and gate dielectrics, respectively. The source and drain electrodes based on gold were prepared by photolithography. The channel length and width were 9 μm and 325 μm, respectively. A hole transporting material containing different additives (15 mg/ml, in chlorobenzene) was spin-coated its surface in a glove-box and encapsulated before the measurements. The I-V characteristics were obtained on a Keithley SCS 4200 in air and the linear region mobility was calculated according to the following formula:

$$\mu = \frac{\partial I_{DS}}{\partial V_{GS}} \frac{L}{W}$$

Here, the $I_{DS}$ is the current collected by drain electrode and $V_{GS}$ is gate voltage, $L$ is the channel length and $W$ is the channel width. The $C_i$ is the captaincy of gate dielectrics and $V_{DS}$ is the voltage between drain and source.

The XRD experiment was performed on a Rigaku SmartLab X-Ray diffractometer equipped with a D/teX Ultra detector. The measurement employed the Cu-Kα line focused radiation at a 9 kW (45 kV, 200 mA) power using a 0.02° 2θ step scan from 3.0–30.0° with a scanning speed of 10° min$^{-1}$. 
Figure S8. The I-V characteristics of field-effect transistor devices (a–c) and XRD (d) of different HTL layers. The output curves of H-1 (a) and H-4 thin films (b), and its corresponding transfer curves (c).

6. Photoemission yield spectroscopy

Figure S9. Photoemission spectra of different P3HT thin-films, (a) H-1 (black square, pristine P3HT) and H-3 (red circle, P3HT doped with Li–TFSI and D-TBP), and (b) H-2 (green circle, P3HT doped with Li–TFSI) and H-4 (blue square, P3HT mixed with D-TBP) coated on ITO substrate. The HOMO level was estimated from the intersection of base line (black) and liner fit lines.

Figure S10. Photoemission spectrum of perovskite thin-film coated on ITO substrate.
7. Solar cell fabrication and measurement

An indium tin oxide (ITO) layer on the glass substrate used for this study was 145 nm thick with a sheet resistance of 8 \( \Omega \)/square. The surface roughness, \( R_m \), was 0.7 nm and the \( R_{\text{max}} \) was 8.1 nm. Prior to the formation of the buffer layer, the patterned ITO glass was ultrasonically cleaned using a surfactant, rinsed with water, and then finally given UV–ozone treatment. A 45-nm thick electron-transporting layer TiO\(_x\) was deposited by spin-coating (3000 rpm for 30s) of the precursor solution (see materials section) and annealed at 500 °C for 30 min in air atmosphere. To form the CH\(_3\)NH\(_3\)PbCl\(_x\)I\(_{3-x}\) layer, a 20 wt% precursor solution was spin-coated on the TiO\(_x\) layer at 500 rpm for 60s and annealed at 95 °C for 100 min in a nitrogen-filled glove box. The hole-transporting layer (see materials section) was then deposited by spin coating (2500 rpm for 30s). The top electrode (Ag, 150 nm) was deposited through a metal shadow mask, which defined a 2 mm stripe pattern perpendicular to the ITO stripe. Finally, the fabricated cell was encapsulated with backing glass using a UV-curable resin under nitrogen atmosphere.

The encapsulated cells were subjected to \( J–V \) measurements under both dark and irradiated conditions. Current–voltage sweeps were taken on a Keithley 2400 source measurement unit controlled by a computer. The light source used to determine the PCE was an AM1.5G solar simulator system (Sumitomo Heavy Industries Advanced Machinery) with intensity of 100 mW/cm\(^2\). The solar cells were masked with a metal aperture to define the active area, typically 4 mm\(^2\). The details of \( J–V \) curve test were as follows: step-size, 0.01V; dwelling time, 0.01s; the scanning range from 1.2 V to –0.3 V. For the external quantum efficiency measurement, a constant power mode was employed using monochromatized photons from halogen or xenon lamps. And for the estimation of IQE spectrum, one-time reflection spectrum from the cell was measured by V-670 spectrophotometer.

![IQE and reflectance spectra](image)

**Figure S11.** The IQE and reflectance spectra of optimized perovskite solar cells using hole-transporting H-3.