Supporting Information

Synergetic Effects of Electrochemical Oxidation of Spiro-OMeTAD and Li\(^+\) Migration in Improving the Performance of n-i-p Type Perovskite Solar Cells

Changzeng Ding, Rong Huang, Christian Ahläng, Jian Lin, Lianping Zhang, Dongyu Zhang, Qun Luo, Fangsen Li, Ronald Österbacka, * Chang-Qi Ma *

1. proposed oxidation mechanism reported in the literature:

\[
\text{Dye} + \text{hv} \rightarrow \text{Dye}^* \rightarrow \text{Dye}^+ + e^- (\text{TiO}_2) \quad (1)
\]

\[
e^- (\text{TiO}_2) + \text{O}_2 \rightarrow \text{O}_2^- \quad (2)
\]

\[
\text{Dye}^+ + \text{Spiro-OMeTAD} \rightarrow \text{Spiro-OMeTAD}^+ + \text{Dye} \quad (3)
\]

**Scheme S1.** proposed oxidation mechanism of Spiro-OMeTAD in solid state dye sensitized solar cells.\(^1\)

\[
\text{Spiro-OMeTAD} + \text{O}_2 = \text{Spiro-OMeTAD} \cdot \text{O}_2 \quad (4)
\]

\[
\text{Spiro-OMeTAD} \cdot \text{O}_2 + \text{LiTFSI} = \text{Spiro-OMeTAD}^+ \text{TFSI}^- + \text{Li}_x\text{O}_y \quad (5)
\]

**Scheme S2.** proposed oxidation mechanism of Spiro-OMeTAD by Snaith et al.\(^2\)

Light Wavelength: 380-450nm

\[
\text{Spiro-OMeTAD} + \text{O}_2 \xrightarrow{\text{hv}} \text{Spiro-OMeTAD}^+ \text{O}_2^{-} \\
\text{Spiro-OMeTAD}^+ \text{O}_2^- + \text{Li}^+ \text{TFSI}^- \rightarrow \text{Spiro-OMeTAD}^+ \text{TFSI}^- + \text{Li}_x\text{O}_y
\]

Light Wavelength: $>450$nm

\[
\text{Perovskite} + \text{O}_2 \xrightarrow{\text{hv}} \text{Perovskite}^+ \text{O}_2^- \\
\text{Perovskite}^+ \text{O}_2^- + \text{Spiro-OMeTAD} \rightarrow \text{Perovskite} + \text{Spiro-OMeTAD}^+ \text{O}_2^- \\
\text{Spiro-OMeTAD}^+ \text{O}_2^- + \text{Li}^+ \text{TFSI}^- \rightarrow \text{Spiro-OMeTAD}^+ \text{TFSI}^- + \text{Li}_x\text{O}_y
\]

**Scheme S3.** proposed oxidation mechanism of Spiro-OMeTAD by Meng et al.\(^3\)
**Figure S1.** Statistical graph of changes in device performance and subsequent oxidation treatment time with fresh devices. (a) Voc, (b) Jsc, (c) FF, (d) PCE.

**Figure S2** Comparison of the current density-voltage (J-V) curves of the same cell as shown in Figure 1b (a) and Figure 1c (b) with multiple scan.

**Figure S3.** The time-dependent curves of device performance parameters under different oxidation conditions (a) Voc (b) Jsc (c) FF (d) PCE
Figure S4. UV-Vis absorption spectra of (a) Glass/Spiro-OMeTAD (50% Li-TFSI:t-BP); (b) Glass/Spiro-OMeTAD (50% Li-TFSI:t-BP)/Ag; (c) Glass/SnO2/Spiro-OMeTAD (50% Li-TFSI:t-BP) films exposure in 30%RH air for different times. (d) Comparison of absorbance changes of the Spiro-OMeTAD films with or without SnO2 layer.
Figure S5. Current density-voltage (J-V) curves of Pre-oxidation cells in the dark and with light illumination.

Figure S6. Statistical graph of changes in device performance and subsequent oxidation treatment time after pre-oxidation .(a) Voc, (b), Jsc, (c) FF, (d) PCE.
**Figure S7.** Water vapor transmission rate (WVTR) of PET (125 μm)/Ag (x nm) film tested at 100%RH atmosphere

**Figure S8** The variation of performance of devices with different thickness of Ag electrode during oxidation process. Note that all the devices were pre-oxidized for 5 h in air with control RH of 30% in the dark.
Figure S9. (a) PL-mapping of perovskite solar cells during the oxidation process in 30% RH air atmosphere, and the active area of solar cell is 1.21 cm². (b) J-V characteristics of the cell upon oxidation are also included.
Figure S10 Current density-voltage (J-V) curves before and after LBIC test under different oxidation conditions a) Fresh, b) Pre-oxidation, c) Post-oxidation.

Figure S11. the distribution of Li⁺ in ITO/Spiro/Ag films before and after oxidation in 3D configuration
**Figure S12.** The evolution of J-V curves within a week for the optimized cell storage in dark in glove box.

**Figure S13.** TOF-SIMS results of (a) Glass/ITO/SnO$_2$/PVSK and (b) diffusion of Li$^+$ and K$^+$ of the perovskite solar cell upon pre- and post-oxidation process.
Figure S14 The variation of performance of devices doped with different concentrations of LiTFSI with oxidation time. Note that all the devices were pre-oxidized for 5 h in air with control RH of 30% in the dark.

Figure S15. $J-V$ curves of the dopant-free (a) and 50% LiTFSI-doped (b) Spiro-OMeTAD based hole only device upon different oxidation conditions.
**Figure S16.** shows the effect of a change in the Ag work function, assuming that the doping concentration in the Spiro-OMeTAD layer is $3 \times 10^{18} \text{ cm}^{-3}$ and that the SnO$_2$ layer is ideal. Assuming that the Ag work function has a work function of 4.3 eV when it is fresh and goes down to 4.8 eV or lower upon oxidation, this could be the origin of the observed s-shapes.

**Figure S17** Electrical potential at short circuit for the simulation data show in Figure 4 (e). The built-in potential is estimated as the maximum potential difference for each curve.
Table S1. shows the parameters used in the drift-diffusion simulations. For the ideal SnO$_2$, we took the surface recombination velocity for holes to be 0.01 cm/s.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Spiro-OMeTAD</th>
<th>Perovskite</th>
<th>SnO$_2$ (non-ideal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>300</td>
<td>400</td>
<td>50</td>
</tr>
<tr>
<td>Electron transport level (eV)</td>
<td>2.0</td>
<td>3.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Hole transport level (eV)</td>
<td>5.0</td>
<td>5.2</td>
<td>7.0</td>
</tr>
<tr>
<td>Effective density of state (cm$^{-3}$)</td>
<td>$10^{20}$</td>
<td>$5 \times 10^{19}$</td>
<td>$10^{20}$</td>
</tr>
<tr>
<td>Electron mobility (cm$^2$/Vs)</td>
<td>-</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Hole mobility (cm$^2$/Vs)</td>
<td>$5 \times 10^{-5}$</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Relative dielectric constant</td>
<td>3</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Electron trap-assisted recombination lifetime (ns)</td>
<td>10 (at perovskite interface)</td>
<td>100</td>
<td>1 (at perovskite interface)</td>
</tr>
<tr>
<td>Hole trap-assisted recombination lifetime (ns)</td>
<td>1 (at perovskite interface)</td>
<td>10</td>
<td>10 (at perovskite interface)</td>
</tr>
<tr>
<td>Radiative recombination coefficient (cm$^3$/s)</td>
<td>-</td>
<td>$10^{-10}$</td>
<td>-</td>
</tr>
<tr>
<td>Generation rate (cm$^3$·s$^{-1}$)</td>
<td>-</td>
<td>$3.4 \times 10^{21}$</td>
<td>-</td>
</tr>
<tr>
<td>Injection barrier (eV)</td>
<td>0.3 (from Ag)</td>
<td>0.1 (from the ideal SnO$_2$)</td>
<td>0.5 (from ITO)</td>
</tr>
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Table S2. The time-resolved photoluminescence (TRPL) fitting results.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
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</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>22.62</td>
<td>53.99</td>
</tr>
<tr>
<td>Pre-oxidation</td>
<td>7.46</td>
<td>35.46</td>
</tr>
<tr>
<td>Post-oxidation</td>
<td>4.77</td>
<td>29.86</td>
</tr>
</tbody>
</table>
Figure S18 The variation of performance of the solar cells (a) with different oxidation times in 30% RH ambient air. (b) storage in N\textsubscript{2} glove box after post-oxidation for 8 h.

References: