Supporting Information

Modifying Mesoporous TiO$_2$ by Ammonium Sulfonate Boosts Performance of Perovskite Solar Cells

Mengmeng Zhang,† Weiran Zhou,† Wanpei Hu,† Bairu Li,† Qiquan Qiao,‡ and Shangfeng Yang*†

†Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei 230026, China

‡Center for Advanced Photovoltaics, Department of Electrical Engineering and Computer Science, South Dakota State University, Brookings, SD 57007, USA

*Corresponding Author. E-mail: sfyang@ustc.edu.cn
Contents

S1. Materials and characterizations.
S2. Elemental mappings of Ti and S for TEATS modified m-TiO$_2$ film.
S3. XPS survey spectra, N 1s and S 2p XPS spectra.
S4. Determination of work funtion of m-TiO$_2$ and TEATS modified m-TiO$_2$.
S5. $J$-$V$ curves of PVKSCs based on m-TiO$_2$ modified by TEATS with variable concentrations.
S6. PCE histograms of devices based on pristine and TEATS modified m-TiO$_2$ layers.
S7. Comparison of the $V_{oc}$ obtained in this work with the high $V_{oc}$ values of conventional meso-PVKSCs based on CsMAFA perovskite reported in literatures.
S8. Statistic photovoltaic parameters for PVKSC devices.
S10. Surface topographic SEM and AFM height images of CsMAFA perovskite films.
S11. 2D-GIXRD profiles of the CsMAFA perovskite films.
S12. XRD patterns of the CsMAFA perovskite films.
S15. Analysis of time-resolved photoluminescence (TRPL) spectra.
S16. Trap state density within perovskite layers.
S17. I 3d and Br 3d XPS spectra.
S18. Fitting parameters for EIS data.
**SI. Materials and characterizations.**

**Materials:** All the solvents and chemicals were used without further purification unless stated otherwise. Fluorine-doped tin oxide (FTO)-coated glass substrates with a sheet resistance of $13 \pm 1.5 \, \Omega \text{sq}^{-1}$ were purchased from NSG Group, Japan. Lead iodide (PbI$_2$, 99.99%), Tetraethylammonium p-toluenesulfonate (TEATS) were purchased from TCI. Methylammonium bromide (MABr), formamidinium iodide (FAI) and TiO$_2$ paste (30 nm) were purchased from Dyesol. Titanium (IV) isopropoxide, lead bromide (PbBr$_2$, 99.999%) were purchased from Alfa Aesar. Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI), Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene were purchased from Sigma-Aldrich. Other chemicals: Caesium iodide (CsI, Xi’an Polymer Light Technology Corp.), TiCl$_4$ (GR, 99.5%, Aladdin), Spiro-OMeTAD (1 M company).

**Measurements and characterizations:** XPS measurements were conducted on a Thermo ESCALAB 250 instrument with a monochromatized Al Kα X-ray source in vacuum. UV-vis spectroscopy was performed on a UV-vis-NIR 3600 spectrometer (Shimadzu, Japan). The energy band of TiO$_2$ ETL was measured with high resolution synchrotron radiation photoelectron spectroscopy (HR-SRPES) with the excitation source of a photon energy of 40 eV by synchrotron radiation light at the Catalysis and Surface Science station in the National Synchrotron Radiation Laboratory (NSRL), Hefei. AFM measurements were performed by XE-7 scanning probe microscope of Park systems in non-contact mode. SEM images were carried out by a field-emission scanning electron microscope (Zeiss Gemini SEM 500). The photovoltaic performance characterizations were performed using a Keithley 2400 source measurement and an Oriel solar simulator with simulated AM 1.5 irradiation (100 mW·cm$^{-2}$) in ambient condition. The solar simulator with a xenon lamp was calibrated with a National
Renewable Energy Laboratory calibrated reference cell of mono-crystalline silicon (Oriel P/N 91150 V, with KG-5 visible color filter). A mask with 0.10 cm² as defined area size is used to ensure precise measurement. X-ray diffraction (XRD) were carried out on a Rigaku SmartLab X-ray diffractometer with Cu-Kα as radiation source (0.154 nm). EQE measurements were performed on an ORIEL Intelligent Quantum Efficiency 200TM Measurement system. The GIXRD measurements were conducted by using X-ray with a wavelength of 1.24 Å at the BL14B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). A software Fit 2D were applied to analyze the 2D-GIXRD patterns. The steady-state photoluminescence (PL) spectra were performed with an excitation wavelength of 460 nm on an Edinburgh Instruments FLS920 fluorescence spectrometer. The time-resolved photoluminescence (TRPL) spectra were carried out on a Picoquant Gmbh Solea Supercontinuum Laser by the time-correlated single-photon counting method. A picosecond pulsed diode laser with a pulse width of 104 ps at 543 nm is utilized as the excitation light. Impedance spectroscopic measurements (EIS) was recorded on an electrochemical workstation (Autolab 320, Metrohm, Switzerland) in dark with a perturbation of AC 20 mV and a bias voltage of 1.0 V. The frequency range from 1 Hz to 1 MHz was applied. Z-View software was utilized to fit the measured impedance spectra.
**S2. Elemental mappings of Ti and S for TEATS modified m-TiO₂ film.**

**Figure S1.** Elemental mappings of (a) Ti and (b) S based on TEATS modified m-TiO₂ measured by SEM.

**S3. XPS survey spectra, N 1s and S 2p XPS spectra.**

**Figure S2.** XPS survey spectra of the (a) pristine m-TiO₂ and (b) TEATS modified m-TiO₂ based on FTO substrates. The high-resolution (c) N 1s and (d) S 2p XPS spectra.
**S4. Determination of work function of m-TiO<sub>2</sub> and TEATS modified m-TiO<sub>2</sub>.**

The valence band energy of m-TiO<sub>2</sub> and TEATS modified m-TiO<sub>2</sub> with respect to the vacuum level ($E_{VAC} = 0$ eV) are determined by the high resolution synchrotron radiation photoelectron spectroscopy (HR-SRPES) at the Catalysis and Surface Science station in the National Synchrotron Radiation Laboratory (NSRL), Hefei. The corresponding spectra is shown in Fig. 2c. The work function ($W_F$) is determined from the secondary electron threshold as $W_F = h\nu - E_{th}$, where $h\nu$ and $E_{th}$ are the photon energy of excitation light (40 eV) and the secondary electron threshold energy, respectively. The secondary electron threshold energy $E_{th} = h\nu - W_f$ (instrument) - $eV_{bi}$ - $E_k$, where $E_k$ is kinetic energy, $W_f$ (instrument) is the work function of the instrument (4.3 eV), $V_{bi}$ is the applied bias to the sample (-5 V).

**S5. J-V curves of PVKSCs based on m-TiO<sub>2</sub> modified by TEATS with variable concentrations.**

![Figure S3. J-V curves of the champion PVKSC devices modified by TEATS with various concentrations scanned in the reverse direction under AM 1.5G solar simulator (100 mW cm<sup>-2</sup>) in air.](image)


Table S1. Photovoltaic parameters of the champion PVKSC devices modified by TEATS with various concentrations.

<table>
<thead>
<tr>
<th>TEATS (mg/ml)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω·cm$^2$)</th>
<th>$R_{sh}$ (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>1.12</td>
<td>23.00</td>
<td>74.33</td>
<td>19.14</td>
<td>5.70</td>
<td>3833.82</td>
</tr>
<tr>
<td>2</td>
<td>1.14</td>
<td>23.22</td>
<td>75.32</td>
<td>19.94</td>
<td>4.28</td>
<td>3770.17</td>
</tr>
<tr>
<td>4</td>
<td>1.16</td>
<td><strong>23.62</strong></td>
<td><strong>75.57</strong></td>
<td><strong>20.69</strong></td>
<td><strong>4.42</strong></td>
<td><strong>4667.96</strong></td>
</tr>
<tr>
<td>8</td>
<td>1.13</td>
<td>23.57</td>
<td>73.22</td>
<td>19.57</td>
<td>5.86</td>
<td>3590.83</td>
</tr>
<tr>
<td>12</td>
<td>1.13</td>
<td>23.18</td>
<td>72.09</td>
<td>18.93</td>
<td>6.63</td>
<td>2886.14</td>
</tr>
</tbody>
</table>

S6. PCE histograms of devices based on pristine and TEATS modified m-TiO$_2$ layers.

![PCE histograms of devices based on pristine and TEATS modified m-TiO$_2$ layers.](image)

Figure S4. PCE histograms of devices based on pristine m-TiO$_2$ and TEATS modified m-TiO$_2$ ETLs.
Comparison of the $V_{oc}$ obtained in this work with the high $V_{oc}$ values of conventional meso-PVKSCs based on CsMAFA perovskite reported in literatures.

**Figure S5.** $J$-$V$ curve of device with the highest $V_{oc}$ based on TEATS modified m-TiO$_2$ ETL.

**Figure S6.** Comparison of the $V_{oc}$ obtained in this work with the high $V_{oc}$ values of conventional meso-PVKSCs based on CsMAFA perovskite reported in literatures.
S8. Statistic photovoltaic parameters for PVKSC devices.

![Box plots for PCE, Voc, Jsc, and FF](image)

**Figure S7.** Statistical distributions of the photovoltaic parameters of (a) PCE, (b) Voc, (c) Jsc and (d) FF for devices based on pristine m-TiO2 and TEATS modified m-TiO2.


![J-V curves](image)

**Figure S8.** The J-V curves of the best performance devices based on (a) pristine m-TiO2, (b) TEATS modified m-TiO2 in different scan direction.
Table S2. Photovoltaic parameters of the best performance devices based on the pristine m-TiO₂ and TEATS modified m-TiO₂ films in different scan directions with 0.1 V/s scan rate.

<table>
<thead>
<tr>
<th>Scanning direction</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>R&lt;sub&gt;s&lt;/sub&gt; (Ω·cm²)</th>
<th>R&lt;sub&gt;sh&lt;/sub&gt; (Ω·cm²)</th>
<th>Hysteresis index&lt;sup&gt;a&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o-reverse</td>
<td>1.119</td>
<td>23.00</td>
<td>74.33</td>
<td>19.14</td>
<td>5.70</td>
<td>3833.82</td>
<td>8.4</td>
</tr>
<tr>
<td>w/o-forward</td>
<td>1.097</td>
<td>22.98</td>
<td>69.60</td>
<td>17.54</td>
<td>6.79</td>
<td>1976.76</td>
<td></td>
</tr>
<tr>
<td>TEATS-reverse</td>
<td>1.159</td>
<td>23.62</td>
<td>75.57</td>
<td>20.69</td>
<td>4.42</td>
<td>4667.96</td>
<td>4.9</td>
</tr>
<tr>
<td>TEATS-forward</td>
<td>1.156</td>
<td>23.60</td>
<td>72.07</td>
<td>19.67</td>
<td>5.30</td>
<td>3142.43</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Hysteresis index = [PCE(reverse) - PCE(forward)]/PCE(reverse)

S10. Surface topographic SEM and AFM height images of CsMAFA perovskite films.

Figure S9. (a-d) Surface topographic SEM images of perovskite films deposited on (a) pristine m-TiO₂, (b) 2 mg/ml TEATS modified m-TiO₂, (c) 4 mg/ml TEATS modified m-TiO₂, (d) 8 mg/ml TEATS modified m-TiO₂. (e-h) The corresponding AFM height images (3 μm × 3 μm) of perovskite films. (i-l) Histograms of grain size distributions of CsMAFA perovskite films spin-coated on the (i) pristine, (j) 2 mg/ml TEATS modified, (k) 4 mg/ml TEATS modified, (l) 8 mg/ml TEATS modified m-TiO₂ estimated from the SEM images using Nano measurer 1.2 software.
**S11. 2D-GIXRD profiles of the CsMAFA perovskite films.**

![2D-GIXRD profiles of the CsMAFA perovskite films deposited on (a) pristine m-TiO₂, (b) 2 mg/ml TEATS modified m-TiO₂, (c) 4 mg/ml TEATS modified m-TiO₂, and (d) 8 mg/ml TEATS modified m-TiO₂ substrates.](image)

**Figure S10.** 2D-GIXRD profiles of the CsMAFA perovskite films deposited on (a) pristine m-TiO₂, (b) 2 mg/ml TEATS modified m-TiO₂, (c) 4 mg/ml TEATS modified m-TiO₂, and (d) 8 mg/ml TEATS modified m-TiO₂ substrates.

![Intensity vs. Azimuth plots for (a) w/o TEATS, (b) 2 mg/ml TEATS, (c) 4 mg/ml TEATS, and (d) 8 mg/ml TEATS.](image)

**Figure S11.** (a) The (001) and (011) peaks obtained by azimuthally integrating peaks in the 2D-GIXRD patterns. (b) The radially integrated intensity plots along the ring at q ≈ 10 nm⁻¹ for the corresponding perovskite films.
S12. XRD patterns of the CsMAFA perovskite films.

![XRD patterns of the CsMAFA perovskite films](image)

**Figure S12.** XRD patterns of the perovskite films deposited on pristine m-TiO$_2$ and TEATS modified m-TiO$_2$ substrates.


![Absorption spectra of CsMAFA perovskite films](image)

**Figure S13.** Absorption spectra of CsMAFA perovskite films deposited on pristine m-TiO$_2$ and TEATS modified m-TiO$_2$ substrates.

We investigated the effect of TEATS modification of m-TiO$_2$ on the carrier mobility based on Mott-Gurney law [Equation (S1)], for which the $J$-$V$ traces showed a quadratic dependence ($I \propto V^{n=2}$) called Child’s regime:\(^1\)

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 E^2 \mu \left( \frac{V^2}{L^3} \right)$$  \hspace{1cm} (S1)

Where the $J$ is current density in dark and $\mu$ is carrier mobility, $L$ is the thickness of the CsMAFA perovskite film (450 nm). According to equation (S1), the electron mobility of $9.24 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $1.58 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ are obtained for the pristine and TEATS modified m-TiO$_2$.

S15. Analysis of time-resolved photoluminescence (TRPL) spectra.

To gain a further understanding of the steady-state PL results, we measured the time-resolved photoluminescence (TRPL) spectra of the CsMAFA perovskite film deposited on pristine and TEATS modified m-TiO$_2$. The excitation source was a 532 nm picosecond laser pulse which was filtered from a supercontinuum generation. The TRPL spectrum can be fitted by a bi-exponential decay function as shown in equation (S2):\(^2\)

$$f(t) = A_1 \cdot \exp\left(\frac{-t}{\tau_1}\right) + A_2 \cdot \exp\left(\frac{-t}{\tau_2}\right) + B$$  \hspace{1cm} (S2)

Where $A_1$, $A_2$, $\tau_1$, $\tau_2$ and $B$ are the decay amplitude, the decay lifetime, and a constant for the baseline offset, respectively. The fast decay lifetime, $\tau_1$, indicates that the PL quenching originated from the m-TiO$_2$/perovskite interfacial charge transfer; while the slow decay lifetime, $\tau_2$, represented the non-radiative recombination of trapped charges within perovskite layers. The short lifetime $\tau_1$ is a decay component related to the charge trapping process, and the long lifetime $\tau_2$ as a component of the de-trapping process or carrier recombination process. The average decay time ($\tau$) was calculated according to the formula $\tau = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$. The fitting results are listed in Table S3.
Table S3. Time constants in TRPL determined by bi-exponential fittings measured on glass, m-TiO$_2$ and TEATS modified m-TiO$_2$ films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>glass</td>
<td>0.27</td>
<td>6.81</td>
<td>0.55</td>
<td>46.41</td>
<td>43.75</td>
</tr>
<tr>
<td>w/o TEATS</td>
<td>0.56</td>
<td>4.13</td>
<td>0.44</td>
<td>24.70</td>
<td>21.09</td>
</tr>
<tr>
<td>with TEATS</td>
<td>0.64</td>
<td>3.61</td>
<td>0.38</td>
<td>21.92</td>
<td>17.94</td>
</tr>
</tbody>
</table>

S16. Trap state density within perovskite layers.

An electron-only device with a structure of FTO/c-TiO$_2$/m-TiO$_2$/TEATS/CsMAFA perovskite/PCBM/Ag was fabricated to determine the trap density of the perovskite layer. The corresponding $J$-$V$ curve for the devices based on pristine and TEATS modified m-TiO$_2$ are presented in Figure 5d. At low bias voltage, $J$-$V$ characteristics is linearly dependent, indicating an ohmic response. When the bias voltage exceeds the kink point, the current density increases nonlinearly, representing where the trap-states are completely filled, the corresponding bias voltage at the kink point is defined as the trap-filled limit voltage ($V_{TFL}$), and the trap-state density ($n_t$) can be determined through equation S3:  

$$ n_t = \frac{V_{TFL}^2 \varepsilon \varepsilon_0}{eL^2} $$  \hspace{1cm} (S3)

Where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ is the relative dielectric constant of perovskite (For FAPbI$_3$, $\varepsilon$=46.9), $e$ is the elementary charge of the electron, and $L$ is the perovskite film thickness. The $V_{TFL}$ of the perovskite layers with m-TiO$_2$ and TEATS modified m-TiO$_2$ as ETLs are determined to be 0.30 V and 0.18 V, respectively, corresponding to a trap-state density ($n_t$) of the perovskite film of $4.25 \times 10^{15}$ cm$^{-3}$ (m-TiO$_2$) and $2.55 \times 10^{15}$ cm$^{-3}$ (TEATS modified m-TiO$_2$), confirming that the trap-states within perovskite layer is effectively passivated.
**S17. I 3d and Br 3d XPS spectra.**

![Figure S14](image)

Figure S14. (a) I 3d, (b) Br 3d of XPS spectra based on pristine perovskite and TEATS treated perovskite deposited on m-TiO$_2$.

**S18. Fitting parameters for EIS data.**

The influence of TEATS modification on the interfacial charge transport behavior of the devices was investigated by using the electrochemical impedance spectroscopy (EIS). The Nyquist plots of devices based on m-TiO$_2$ measured in the dark under a reverse potential of 1.0 V (near the open circuit potential) are compared in Figure 6b. Based on the equivalent circuit model, the data in the Nyquist plot is separated into two R-CPE arcs, consisting of a resistor $R_s$ (series resistance, which is defined as the starting point at the real part of the Nyquist plot) connected with two parallel R-CPE elements. The $R_{co}$ (contact resistance) is characterized by the high-frequency feature, which is associated with the ETL/perovskite interface. The recombination resistance ($R_{rec}$, which is sensitively dependent on the recombination properties) and the non-ideal chemical capacitances ($CPE_1, CPE_2$) of the system are determined by the lower frequency element. The parameters used for fitting are summarized in Table S4.
Table S4. Parameters employed for the fitting of the impedance spectra of devices based on the pristine m-TiO₂ and TEATS modified m-TiO₂ films.

<table>
<thead>
<tr>
<th>Device</th>
<th>(R_s) (Ω•cm²)</th>
<th>(R_{co}) (Ω•cm²)</th>
<th>CPE1-T (F/cm²)</th>
<th>CPE1-P (F/cm²)</th>
<th>(R_{rec}) (Ω•cm²)</th>
<th>CPE2-T (F/cm²)</th>
<th>CPE2-P (F/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>23.53</td>
<td>29.71</td>
<td>5.557E-8</td>
<td>1.035</td>
<td>1340</td>
<td>1.0912E-8</td>
<td>1.015</td>
</tr>
<tr>
<td>TEATS</td>
<td>20.77</td>
<td>25.56</td>
<td>2.893E-7</td>
<td>0.99085</td>
<td>2670</td>
<td>2.1797E-8</td>
<td>0.992</td>
</tr>
</tbody>
</table>


Figure S15. Stabilities of devices based on m-TiO₂ with and without TEATS modification stored in ambient condition without encapsulation (temperature: 25 °C, relative humidity: 30%). Dependence of device parameters (a) PCE, (b) \(V_{oc}\), (c) \(J_{sc}\), (d) FF on the storage time.
References


