Modulating perovskite crystallization process towards highly efficient and stable perovskite solar cells via MXene quantum dots modified SnO$_2$

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Methods

Materials

Methylammonium Iodide (CH$_3$NH$_2$I), Lead chloride (PbI$_2$, 99.99%), Spiro-OMeTAD, Anhydrous dimethyl sulfoxide (DMSO), ethanol, and isopropanol and γ-butyrolactone were purchased from Sigma Aldrich. HNO$_3$, H$_2$SO$_4$, Na$_2$S$_2$O$_3$ and acetone Sinopharm Chemical Reagent Co., Ltd. All these of these chemicals are used directly without any purification.

Synthesis of S and N co-doped MXene quantum dots (S, N-MQDs).

A mixture of HNO$_3$ and H$_2$SO$_4$(1:3) was used to dissolve the Ti$_3$C$_2$ powder by heating it at 100 °C for 12 h. The resulting solution was further diluted with 100 mL deionized water and cooled to 0 °C by an ice-bath. NaOH was added portion wise to the obtained products until the pH reached to ∼7. To obtain S, N-MQDs, 0.05 g of Na$_2$S$_2$O$_3$ and 200 µL of NH$_3$·H$_2$O were added to 20 mL of treated Ti$_3$C$_2$ in a 50 mL Teflon-lined, stainless-steel autoclave, and the mixture was heated at 150°C for 12 h. Thereafter, a 1000 Da dialysis membrane was used to first dialyze the reaction mixture for 2 days for isolation and purification. Subsequently, further purification was carried out by using a dialysis bag against ultra-pure water.

Preparation of MQDs-SnO$_2$ precursor solution.

The synthesized S, N-MQDs powder was firstly dispersed in deionized water at a concentration of 1 mg/ml. The resulting solution was then added into an aqueous solution of SnO$_2$ at a mass ratio (wt.%) of 0.0050 mg/ml, 0.0075mg/ml, 0.0100mg/ml, and 0.0200 mg/ml followed by ultrasonication for over 50 min.

Preparation of perovskite precursor.

A mixed organic cation solution (PbI$_2$ 1.1M; MABr 0.05M; MACl 0.26 M; FAI 0.9 M; CsI 0.05 M) were dissolved in a (0.6 mL) mixed solvent of DMF: DMSO = 4:1. The solution was placed on a hot plate at 60 °C for 2 h. Finally, the solution was filtered just before the deposition of the perovskite layer.

Device fabrication

The ITO glasses were sequentially cleaned with deionized water, acetone, ethanol, and isopropanol with ultrasonication for each 20 minutes respectively. After 15 min of UV-ozone treatment, the SnO$_2$ solution (Alfa-aesar) or the corresponding MQDs-SnO$_2$ solution were spin-coated on the ITO substrates at 3000 rpm for 40 s followed by annealing at 150 °C for 20 min. Thereafter, the perovskite precursor solution was dropped on the treated SnO$_2$ layer, followed by spin-coating at 2000 rpm for 10 s and 6000 rpm for 30 s. Chlorobenzene (CB) was used as an antisolvent in the last 10 s. As-deposited films were later transferred onto a hot plate and then annealed at 100 °C for 10 min and at 150°C for another 20 min. Spiro-OMeTAD solution was prepared using previously reported protocol (1). The
Spiro-OMeTAD chlorobenzene solution was spin-coated onto the perovskite layer at 5000 rpm for 40 s. The device was put in a dry air box overnight (humidity of 20% at room temperature). Finally, the semi-finished devices were transferred into a vacuum chamber for the deposition of MoO$_3$ (3 nm) and then the Au (60 nm) electrode under a base pressure of $4.0 \times 10^{-4}$ Pa. The active area of each device was 0.05 cm$^2$. After fabrication, all of the devices were kept unencapsulated in the glovebox for further measurements.

**Characterization**

The photovoltaic performance was measured by 2400 Series Source Meter (Keithley Instruments) under an AM 1.5G solar simulator (XES-301S, SAN-EI) which has been calibrated by a NREL standard Si cell. Incident photon-to-current conversion efficiency (IPCE) measurements were collected by the QE-R (Solar Cell Scan 100, Zolix instruments. Co. Ltd.). A Quanta 200 FEG was used to obtain the field-emission scanning electron microscope (SEM) images. The grazing incidence X-ray diffraction (GIXRD) and in-situ GIXRD were performed at the Shanghai Synchrotron Radiation Facility (SSRF) using X-ray with a wavelength of 1.24 Å. Two-dimensional XRD patterns were acquired by a MarCCD at a distance of ~263 mm from the sample with an exposure time of 20 s. The grazing incidence angle of 0.40° was adopted. Optical absorption spectrum of perovskite films was measured by using an ultraviolet spectrophotometer (U-418 3010, Hitachi High-Technologies, Japan). Photoluminescence spectra were measured by using fluorescence spectrophotometer (Fluoromax 4, HORIBA Jobin Yvon, United States). Time-resolved PL spectra were collected by using FLS980 Spectrometer (Edinburgh instruments). For the ETLs, the XPS and UPS were done at the photoemission spectroscopy (4B9B) beamline in the Beijing Synchrotron Radiation Facility. For perovskite films, the UPS spectra were collected by a SPECS PHOIBOS 100 hemispherical analyzer which is excited by an unfiltered He I (21.20 eV) gas discharge lamp. Surface topographies (AFM) were imaged using an atomic force microscope (Keysight 5500). A focused ion beam (FIB) equipped with high resolution scanning electron microscopy (HR-TEM) were used to measure the interfaces of perovskite/ETLs.

**Explanation of the movies**

Supplementary movies S1 and S2 display the evolution of 2D-GIXRD patterns fabricated on pristine SnO$_2$ and MQDs-SnO$_2$ ETLs during the whole spin-coating process, respectively.

**Reference**

Supporting figures and tables

Figure S1. TEM image of N, S, co-doped Ti$_3$C$_2$T$_x$ quantum dots (MQDs).
Figure S2. TEM images of a solution processed SnO$_2$ (a) and MQDs-SnO$_2$ (concentration of MQDs is 0.0075mg/ml) nanocrystals (b), which are deposited on copper mesh respectively. A photo image of the SnO$_2$ and MQDs-SnO2 nanoparticle solutions (c).
Figure S3. The elements C, O and Sn EDX mappings of MQDs-SnO$_2$ nanocrystals film.
Figure S4. SEM (a, b) and AFM (c, d) images of SnO$_2$ and SnO$_2$-MQDs (0.0075mg/ml) films, respectively.
Figure S5. (a) $J-V$ characteristics of electron-only devices based on MQDs-SnO$_2$ and SnO$_2$ ETLs, from which their electron mobility was calculated from the SCLC model. (b) Conductivity properties of SnO$_2$ films with and without MQDs.
Figure S6. GIXRD patterns of SnO$_2$ and SnO$_2$-MQDs (0.0075mg/ml) films.
Figure S7. Optical absorptions of SnO$_2$ and SnO$_2$-MQDs (0.0075mg/ml) films.
Figure S8. XPS spectra of SnO$_2$ and SnO$_2$-MQDs (0.0075mg/ml) films.
Figure S9. (a) UPS spectra of SnO$_2$ and SnO$_2$-MQDs (0.0075mg/ml) films; (b) UPS spectra of perovskite films grown on SnO$_2$ and SnO$_2$-MQDs (0.0075mg/ml) films respectively; (c) Band alignments of perovskite films grown on SnO$_2$ and SnO$_2$-MQDs (0.0075mg/ml) films respectively.
Figure S10. A statistical distribution of the grain sizes for perovskites films fabricated on SnO$_2$ and MQDs-SnO$_2$ ETLs.
Figure S11. Integrated 1D-GIXRD spectra of the perovskite films deposed on SnO$_2$, RCQs-SnO$_2$ and MQDs-SnO$_2$ substrates after the first 30 seconds spin-coating before anti-solvent treatments.
Figure S12. 2D-GIXRD patterns of the perovskite films recorded at five different time intervals (0.5, 8.5, 16.5, 24.5, and 30.5 minutes) during the annealing process.
Figure S13. In-situ GIXRD study on the thermal stability of perovskite films. (a-b) *in-situ* GIXRD patterns for the perovskite films deposited on SnO$_2$ and MQDs-SnO$_2$ ETL substrates with 40-60% RH at 100 °C *versus* time and (c) integrated (110) diffraction peaks for the perovskite films deposited on SnO$_2$ and MQDs-SnO$_2$ ETL substrates with 40-60% RH at 100 °C *versus* time.
Figure S14. Cross-sectional SEM images of perovskite films on (a) SnO$_2$ ETL and (b) MQDs-SnO$_2$ ETLs. Scale bar is 1µm.
Figure S15. Cross-sectional HR-TEM images of the perovskite/SnO$_2$ ETL/ITO interface (a, b) and the perovskite/MQDs-SnO$_2$ ETL/ITO interface (c, d), respectively.
Figure S16. $J$-$V$ curves of the MQDs-SnO$_2$-based PSCs with different MQDs doping ratios as shown in the inset.
Figure S17. Statistics of the photovoltaic parameters: $V_{OC}$, $J_{SC}$, FF, and PCE of PSCs employing different concentration MQDs doped SnO$_2$ ETL.
Figure S18. Thermal stability test of the reference and target PSCs by annealing them at 60 °C for 120 hours and recording their PCEs at different times.
Table S1. Photovoltaic performance parameters of PSCs employing different MQDs doping concentrations based SnO\textsubscript{2} ETL. Data were collected from 36 devices of each type for the error analysis.

<table>
<thead>
<tr>
<th>Weight ratios</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm\textsuperscript{2})</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tbody>
<tr>
<td>Control</td>
<td>1.127±0.014</td>
<td>23.68±0.059</td>
<td>0.745±0.011</td>
<td>20.39±0.55</td>
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<td>0.0050 mg/ml</td>
<td>1.150±0.011</td>
<td>24.25±0.026</td>
<td>0.769±0.008</td>
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<td>0.0075 mg/ml</td>
<td>1.168±0.009</td>
<td>24.97±0.030</td>
<td>0.776±0.006</td>
<td>22.77±0.41</td>
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<td>0.0100 mg/ml</td>
<td>1.159±0.012</td>
<td>24.64±0.038</td>
<td>0.768±0.006</td>
<td>22.17±0.53</td>
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<tr>
<td>0.0200 mg/ml</td>
<td>1.145±0.016</td>
<td>23.29±0.064</td>
<td>0.739±0.015</td>
<td>20.24±0.71</td>
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Table S2. Photovoltaic performance parameters of champion PSCs with SnO\textsubscript{2} and MQDs-SnO\textsubscript{2} as ETLs.

<table>
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<tr>
<th>ETLs</th>
<th>Scan direction</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm\textsuperscript{2})</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tbody>
<tr>
<td>SnO\textsubscript{2}</td>
<td>Reverse</td>
<td>1.140</td>
<td>24.26</td>
<td>75.8</td>
<td>20.96</td>
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<td></td>
<td>Forward</td>
<td>1.143</td>
<td>24.25</td>
<td>72.1</td>
<td>19.98</td>
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<tr>
<td>MQDs-SnO\textsubscript{2}</td>
<td>Reverse</td>
<td>1.172</td>
<td>24.96</td>
<td>79.8</td>
<td>23.34</td>
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<tr>
<td></td>
<td>Forward</td>
<td>1.174</td>
<td>24.90</td>
<td>79.5</td>
<td>23.23</td>
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Table S3. Photovoltaic performance comparison of champion PSCs based on SnO\textsubscript{2}, RCQs-SnO\textsubscript{2}(our previous report ETL in Ref. 12) and MQDs-SnO\textsubscript{2} ETLs.

<table>
<thead>
<tr>
<th>ETLs</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm\textsuperscript{2})</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO\textsubscript{2}</td>
<td>1.140</td>
<td>24.26</td>
<td>75.8</td>
<td>20.96</td>
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<td>RCQs-SnO\textsubscript{2}</td>
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<td>24.75</td>
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<td>22.26</td>
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<tr>
<td>MQDs-SnO\textsubscript{2}</td>
<td>1.172</td>
<td>24.96</td>
<td>79.8</td>
<td>23.34</td>
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