### **Supporting material**

# Modulating perovskite crystallization process towards highly efficient and stable perovskite solar cells via MXene quantum dots modified SnO<sub>2</sub>

Yingguo Yang<sup>1,2,#,\*</sup>, Haizhou Lu<sup>3,4,#</sup>, Shanglei Feng<sup>1,2,#</sup>, Lifeng Yang<sup>1,2,#</sup>, Hua Dong<sup>5</sup>, Jiaou Wang<sup>6</sup>, Chen Tian<sup>1,2</sup>, Lina Li<sup>1,2</sup>, Hongliang Lu<sup>7</sup>, Jaeki Jeong<sup>3</sup>, Shaik M. Zakeeruddin<sup>4</sup>, Yuhang Liu<sup>4,\*</sup>, Michael Grätzel<sup>4,\*</sup>, Anders Hagfeldt<sup>3,8,\*</sup>

<sup>1</sup>Shanghai Synchrotron Radiation Facility (SSRF), Zhangjiang Lab, Shanghai Advanced Research Institute, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China. <sup>2</sup>University of Chinese Academy of Sciences, Beijing 100049, China

<sup>3</sup>Laboratory of Photomolecular Science, Institute of Chemical Sciences Engineering, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

<sup>4</sup>Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, EPFL, CH-1015 Lausanne, Switzerland.

<sup>5</sup>Key Laboratory for Physical Electronics and Devices of the Ministry of Education & Shaanxi, Xi'an Jiaotong University, China.

<sup>6</sup>Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China.

<sup>7</sup>School of Microelectronics, Fudan University, Shanghai 200433, China.

<sup>8</sup>Current address: Department of Chemistry, Ångström Laboratory, Uppsala University, Box 523, 751 20 Uppsala, Sweden.

<sup>#</sup>These authors contributed equally to this work.

\*Corresponding author. Email: yangyingguo@sinap.ac.cn (Y.Y.); yuhang.liu@epfl.ch (Y.L.); michael.graetzel@epfl.ch (M.G.); anders.hagfeldt@uu.se (A.H.).

#### Methods

#### Materials

Methylammonium Iodide (CH<sub>3</sub>NH<sub>2</sub>I), Lead chloride (PbI<sub>2</sub>, 99.99%), Spiro-OMeTAD, Anhydrous dimethyl sulfoxide (DMSO), ethanol, and isopropanol and γ-butyrolactone were purchased from Sigma Aldrich. HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>(1:3) was used to dissolve the Ti<sub>3</sub>C<sub>2</sub> 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<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and 200  $\mu$ L of NH<sub>3</sub>·H<sub>2</sub>O were added to 20 mL of treated Ti<sub>3</sub>C<sub>2</sub> 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-SnO2 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<sub>2</sub> 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<sub>2</sub> solution (Alfa-aesar) or the corresponding MQDs-SnO<sub>2</sub> 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<sub>2</sub> 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  $0.05 \text{ cm}^2$ . 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 photonto-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). Timeresolved 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<sub>2</sub> and MQDs-SnO<sub>2</sub> ETLs during the whole spin-coating process, respectively.

#### Reference

(1) Meng Li, *et al.* Graphdiyne-modified cross-linkable fullerene as an efficient electron transporting layer in organometal halide perovskite solar cells, *Nano Energy*, **43**, 47–54 (2018).

## Supportting figures and tables



Figure S1. TEM image of N, S, co-doped  $Ti_3C_2T_x$  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- $SnO_2$  nanoparticle solutions (c).



Figure S3. The elements C, O and Sn EDX mappings of MQDs-SnO<sub>2</sub> 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<sub>2</sub> and SnO<sub>2</sub> ETLs, from which their electron mobility was calculated from the SCLC model. (b) Conductivity properties of SnO<sub>2</sub> 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 1 $\mu$ m.



Figure S15. Cross-sectional HR-TEM images of the perovskite/SnO<sub>2</sub> ETL/ITO interface (a, b) and the perovskite/MQDs-SnO<sub>2</sub> ETL/ITO interface (c, d), respectively.



Figure S16. *J*-V curves of the MQDs-SnO<sub>2</sub>-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<sub>2</sub> 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.

Weight ratios	V <sub>oc</sub> (V)	$J_{\rm sc}({\rm mA/cm^2})$	FF	PCE (%)
Control	1.127±0.014	23.68±0.059	0.745±0.011	20.39±0.55
0.0050 mg/ml	1.150±0.011	24.25±0.026	$0.769 \pm 0.008$	21.85±0.53
0.0075 mg/ml	1.168±0.009	24.97±0.030	0.776±0.006	22.77±0.41
0.0100 mg/ml	1.159±0.012	24.64±0.038	0.768±0.006	22.17±0.53
0.0200 mg/ml	1.145±0.016	23.29±0.064	0.739±0.015	20.24±0.71

Table S1. Photovoltaic performance parameters of PSCs employing different MQDs doping concentrations based  $SnO_2$  ETL. Data were collected from 36 devices of each type for the error analysis.

Table S2. Photovoltaic performance parameters of champion PSCs with  $SnO_2$  and  $MQDs-SnO_2$  as ETLs.

ETLs	Scan direction	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
SnO <sub>2</sub>	Reverse	1.140	24.26	75.8	20.96
	Forward	1.143	24.25	72.1	19.98
MQDs-SnO <sub>2</sub>	Reverse	1.172	24.96	79.8	23.34
	Forward	1.174	24.90	79.5	23.23

Table S3. Photovoltaic performance comparison of champion PSCs based on SnO<sub>2</sub>, RCQs-SnO<sub>2</sub>(our previous report ETL in Ref. 12) and MQDs-SnO<sub>2</sub> ETLs.

ETLs	$V_{\rm oc}$ (V) $J_{\rm s}$	<sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
SnO <sub>2</sub>	1.140	24.26	75.8	20.96
RCQs-SnO <sub>2</sub>	1.168	24.75	77.0	22.26
MQDs-SnO <sub>2</sub>	1.172	24.96	79.8	23.34