

Supporting Information

Perovskite Solar Cell with MoS₂ Electron Transport Layer

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EXPERIMENTAL SECTION

Materials. Molybdenum (V) chloride (MoCl_5 , 99.99%), thiourea (99.99%), 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{Bmim}]^+[\text{BF}_4]^-$, 98%), lead (II) iodide 99% (PbI_2), and methyl ammonium iodide (MAI) were purchased from Sigma-Aldrich and used as received. 2,2',7,7'-tetrakis[N-4-methoxyphenyl-N'-2-methoxyphenyl amino]-9,9'-spirobifluorene (po-Spiro-MeOTAD) hole transport material (HTL) was purchased from 1-Material company.

Synthesis of MoS_2 thin film. 25 mM MoCl_5 and 125 mM thiourea were dissolved in 5 mL of $[\text{Bmim}]^+[\text{BF}_4]^-$ under magnetic stirring. After 2 h, argon gas was bubbled through the reaction mixture for 30 min to remove any dissolved O_2 in the reaction mixture. Next, the required amount of the precursor solution was dropped on the polished side of a $1.5 \text{ cm}^2 \text{ p}^{++}$ Si wafer and FTO coated side of a glass substrate of the same size was placed downward over the precursor mixture, followed by thermal annealing for 5 min on a hot plate at $90 \text{ }^\circ\text{C}$. The sandwiched precursor solution was put in a commercial microwave oven. Microwave was irradiated for 30 - 45 s at its minimum power in a single-mode variable-power of 700 W. Afterward, the reaction mixture was allowed to cool down to room temperature naturally in the air. Finally, the samples were washed with DI water and ethanol alternatively several times before drying them in a vacuum desiccator.

Thin film deposition of SnO_2 and TiO_2 . For SnO_2 deposition, the SnO_2 precursor was prepared by dissolving 0.1M of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in ethanol solvent. The prepared solution was magnetically stirred for 48 h at room temperature. SnO_2 film was deposited by spin-coating on a glass/FTO substrate at 2000 rpm for 30 s. After spin coating, substrates were annealed at 180°C for 2 h to remove the residual organic solvents. For TiO_2 deposition, TiO_x precursor was synthesized

with a recipe reported in the literature.¹ The reaction was carried out in dried glassware and under argon atmosphere. 2 mL of titanium (IV) isopropoxide (Aldrich, 99.999%) was mixed with 10 mL of 2-methoxyethanol (Aldrich, 99.9%) and 1 mL of ethanolamine (Aldrich, 99%) in a three-necked flask equipped with a condenser and a thermometer. Then, the mixed solution was stirred at 80°C for 2 h in silicon-oil bath and then heated to 120°C for 2 h. It should be noted that all the chemical compounds were kept in the flask all the time under an inert atmosphere. The TiO_x precursor solution for device fabrication was diluted in anhydrous ethanol with 1:5 (v:v). A thin layer of compact anatase TiO₂ was formed through spin coating the TiO₂ solution on the clean glass/FTO substrates at 4000 rpm for 30 s, followed by a sintering process in a furnace at 500 °C for 30 min.

Solar cell fabrication. The inverted structure of the PSCs was prepared with a stack of glass/FTO/ ETL/photoactive perovskite layer/po-Spiro-MeOTAD/Au. The electrode with the ETL (MoS₂, SnO₂, TiO₂) was transferred into N₂-filled glovebox for deposition of the perovskite layer. For perovskite film deposition, 1.2 M PbI₂ solution was prepared in DMF:DMSO (6:4 v/v %) at 70 °C and another 45 mg/mL MAI solution was prepared in isopropyl alcohol (IPA) at room temperature with overnight stirring in glovebox. The MAPbI₃ perovskite films were prepared by the well-known two-step spin-coating process.² First, the PbI₂ solution was spin-coated at 3000 rpm for 20 s, and dried on hot plate at 60 °C for 5 min. The MAI solution was then spin-coated on the dried PbI₂ film for 30 s, and finally, the spin-coated substrate was immediately transferred to a hot plate of 100 °C. The annealing was maintained for 45 min to form the perovskite material. The solution of hole extracting material was prepared by dissolving 72.3 mg of po-spiro-MeOTAD, 28.8 μL 4-tert-butylpyridine, 17.5 μL of a stock solution (520 mg mL, 1-lithium bis(trifluoromethylsulphonyl)imide in

acetonitrile) in 1.0 mL anhydrous chlorobenzene. The solution was spin-coated at 4000 rpm for 30 s. Finally, Au (80 nm) anode was thermally deposited under high vacuum ($< 2 \times 10^{-6}$ Torr) through a shadow metal mask to create solar cell devices of 0.056 cm².

Characterization of solar cells. The electrical properties were measured with a Keithley 4200 unit under one sun condition in a N₂-filled glovebox. The external quantum efficiency was measured by using a photo-modulation spectroscopy setup (Merlin, Oriel) with monochromatic light from a Xenon lamp. The light intensity dependent current density-voltage (J - V) curves were obtained with a solar simulator setup by varying the light intensity from 10 - 100 mW/cm².

Thin film characterization. The UV-Vis absorption/transmission and PL spectra of the spin-coated films were recorded using a spectrometer (Perkin Elmer, Lambda 1050) and a spectrofluorimeter (Horiba Jobin Yvon NanoLog), respectively. Thin film morphological characterizations like field emission-scanning electron microscope (FE-SEM) images were captured by Hitachi S-4800 FE-SEM system, scanning transmission electron microscopy (STEM, JEM-2100F, and JEM-2011HC, JEOL) at an accelerating voltage of 200 kV, atomic force microscopy (AFM) images were recorded by using a SPA300HV instrument equipped with a SPI3800 controller (Seiko Instruments) and energy dispersive X-ray spectrometry (EDS, INCA X-sight 7421, Oxford Instruments). The Raman spectrum was measured using Micro-Raman spectrometer (Witec Alpha 300 RA Confocal Raman), with the wavelength (532 nm) and spot size (1 μm) of the excitation laser. The time-resolved photoluminescence spectroscopy (TRPL) traces were recorded by using time-correlated single photon counting (TCSPC) system (Hamamatsu/C11367-31). The conditions of the pulsed laser source for the TCSPC

measurements were a wavelength of 464 nm, a repetition rate of 100 kHz, fluence of $\sim 4 \text{ nJ/cm}^2$, and a pulse width of 70 ps. All samples were excited from the bottom perovskite side with an excitation wavelength of 464 nm and an emission wavelength of 770 nm was recorded under ambient conditions.

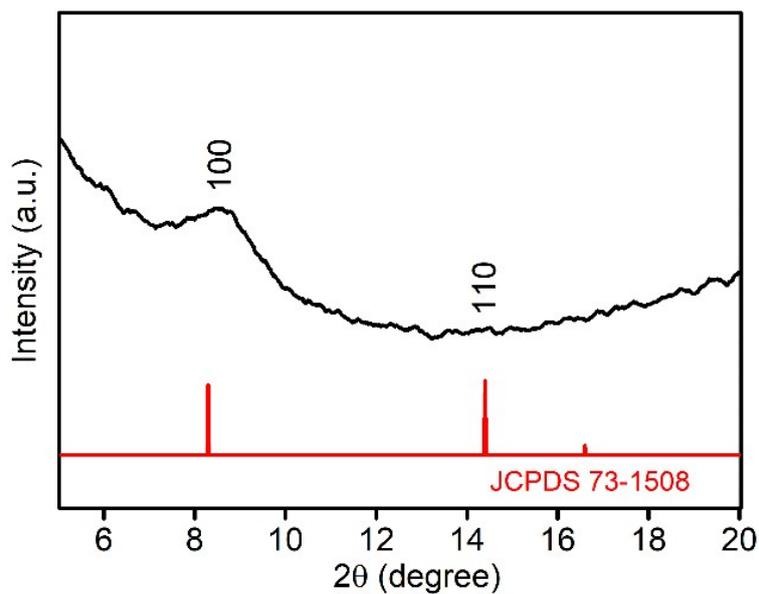


Figure S1. Thin film XRD of the MoS₂ thin film measured over glass substrate.

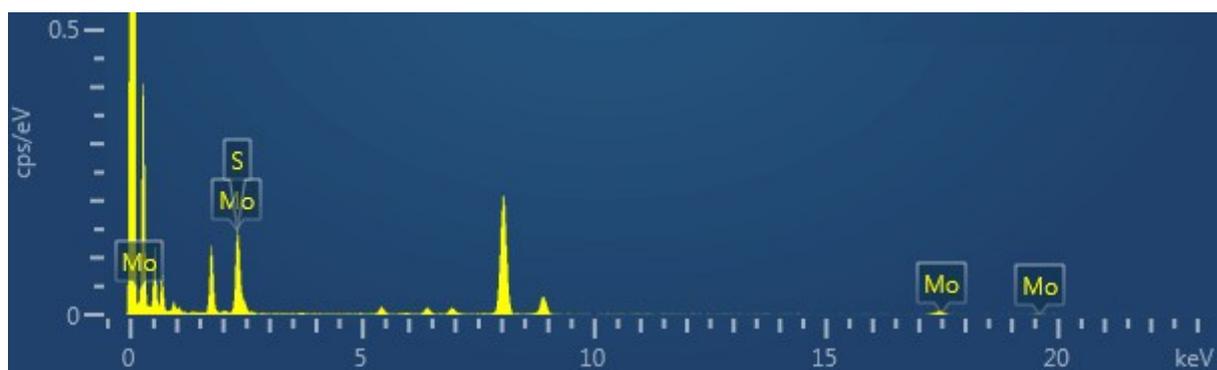


Figure S2. EDS spectrum of the MoS₂ thin film showing the presence of Mo and S as the principle element. The peak due to the supporting Cu grid can be seen around 8 eV.

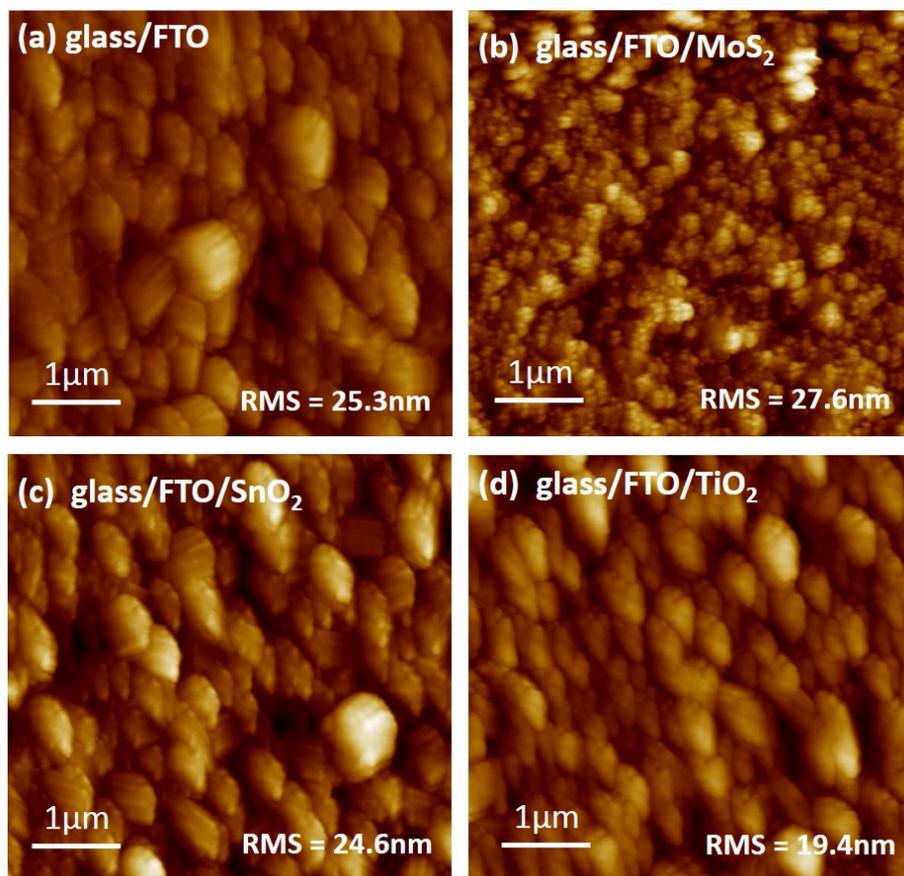


Figure. S3 AFM height images of the different ETL films; (a) Glass/FTO, (b) Glass/FTO/MoS₂, (c) Glass/FTO/SnO₂, and (d) Glass/FTO/TiO₂.

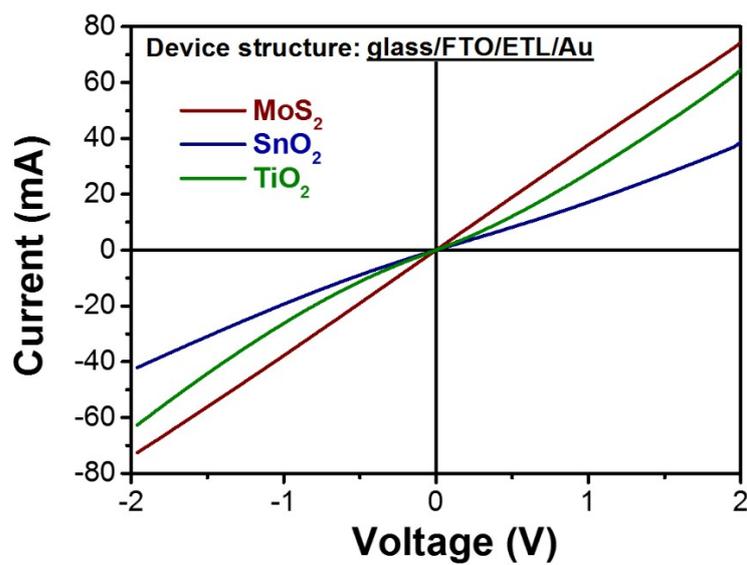


Figure S4. *I-V* characteristics of the Glass/FTO/ETLs/Au devices.

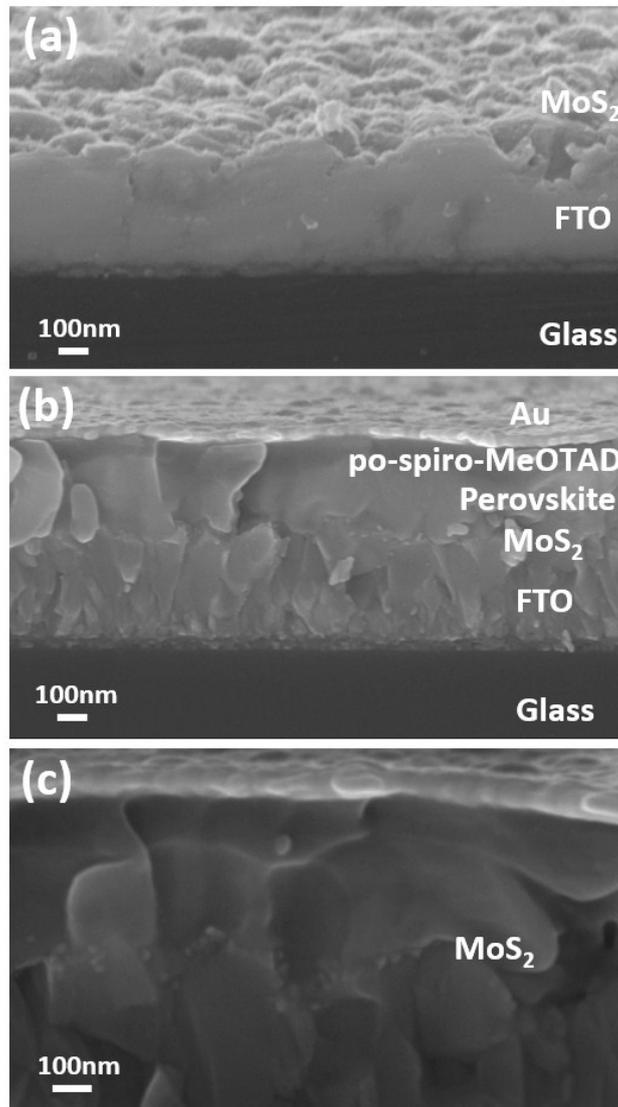


Figure S5. Cross-sectional FESEM of the (a) glass/FTO/MoS₂ substrate (c) glass/FTO/MoS₂/perovskite/po-spiro-OMeTAD/Au device and (c) magnified cross-sectional image of the device.

Table S1. STEM-EDS elemental analysis of MoS₂ thin film.

Element	Line Type	Atomic %
S	K series	66.64
Mo	K series	33.36
Total:		100.00

REFERENCES

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2. Tao, C.; Neutzner, S.; Colella, L.; Marras, S.; Srimath Kandada, A. R.; Gandini, M.; Bastiani, M. D.; Pace, G.; Manna, L.; Caironi, M.; Bertarelli, C.; Petrozza, A., 17.6% stabilized efficiency in low-temperature processed planar perovskite solar cells. *Energy Environ. Sci.* **2015**, *8*, 2365-2370.