Electronic Supplementary Information

Aqueous solution processed MoS₃ as an eco-friendly hole-transport

layer for all-inorganic Sb₂Se₃ solar cells

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Experimental Section

Preparation of MoS₃ Precursor Solution.

 $(NH_4)_2MoS_4$ was dissolved in deionized water with a concentration of 20 mg/mL. The mixture was then stirred at 60 °C in a nitrogen atmosphere for 30 min until completely dissolved. The solution needs to be filtered through a 0.22 µm poly-(tetrafluoroethylene) filter before use.

Device Fabrication.

The FTO glass was sequentially cleaned by ultrasonic wave with water, isopropanol, acetone and ethanol for 30 min in each cleaning step. Then, the cleaned FTO glass was treated with UV-ozone for 15 min before use. The CdS layer was prepared by chemical bath deposition with 0.015 mol/L Cd (NO₃)₂, 1.50 mol/L thiourea and 1.56 mol/L ammonia aqueous solution. The deposition of CdS was conducted at 66 °C for 16 min with the substrate facing down in the growth solution. The deposited CdS layer was then treated with 20 mg/mL CdCl₂ methanol solution by spin coating and annealed in air ambient at 400 °C for 10 min. Sb₂Se₃ layer was deposited on CdS coated FTO glass by vacuum thermal evaporation. $0.3 \text{ g Sb}_2\text{Se}_3$ was weighted to the tungsten boat and the distance between the evaporation source and the substrate was set to 10 cm. The deposition was under a vacuum pressure up to 5×10^{-4} Pa. Before evaporating Sb₂Se₃, the substrate was heated to 315 °C and dwelled for 30 min. The deposition rate was raised to 3~5 nm/s and the final evaporation thickness was controlled at 400 nm. The (NH₄)₂MoS₄ aqueous solution precursor were spin-coated on Sb₂Se₃ film at 3000 rpm for 30 s. Then, the MoS_3 film was then formed by annealing on a preheated plate in a nitrogen glovebox (argon atmosphere, $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) at different temperature for 10min. Au electrodes were finally deposited on the films to complete the device fabrication. The active area of the device was defined as 0.12 cm^2 .

Characterizations and Measurements.

Thermogravimetric analysis (TGA) was used to study the weight loss of (NH₄)₂MoS₄ by a TGA Q5000 instrument under nitrogen atmosphere at a heating rate

of 10 °C/min with temperature increasing from 30 °C to 550 °C. The surface and crosssection morphologies of the Sb₂Se₃ films and MoS₃ films were characterized by Field emission SEM (Hitachi, SU8220). The X-ray diffraction (XRD) patterns of samples were performed on a Bruker Advance D8 diffractometer equipped with Cu Ka radiation $(\lambda = 1.5416 \text{ Å})$, and the samples was tested in silicon wafers. XPS (Thermo ESCALAB, 250Xi) was used to characterise the chemical composition of MoS₃ and Sb₂Se₃ films with an Al K α monochromatized source and a multidetection analyzer under 10⁻⁸ Torr. Atomic Force Microscopy characterization (AFM, Bruker Dimension Edge) was carried out to check the roughness of Sb₂Se₃ with and without MoS₃ as the HTL. UPS (Synchrotron radiation photoemission spectroscopy, He I excitation, 30 eV, referenced to the Femi edge of argon etched gold) was implemented to detect the Femi level and valence band of MoS₃ and Sb₂Se₃ films. Raman spectrum (Horiba JobinYvon, LabRAM HR800) were applied to analyze the chemical bond property of Sb₂Se₃ and MoS₃ with 532 nm excitation wavelength and under a power density of 0.4 mW/ μ m². J-V curve and PCE of Sb₂Se₃ solar cells were measured by a standard xenon lamp solar simulator illumination with a Keithley 2400 digital Source-Meter under AM 1.5G illuminations (100 mW·cm⁻²) in air ambient at room temperature. A halogen lamp single source illumination system combining with a monochromator was used to measure the incident photon-to-current conversion efficiency (IPCE, Model SPIEQ200). Electrochemical impedance spectroscopy (EIS) measurements were performed using the Zahner Mess System PP211 electrochemical workstation at a bias potential of -0.50 V in the dark with the frequency ranging from 100 Hz to 1 MHz. Capacitance-voltage (C-V) measurements were conducted by electrochemical workstation (Zahner Mess Systeme PP211) with a frequency of 100 kHz at room temperature in darkness and the AC amplitude was 5 mV. DC bias voltage was changed from -0.6 to 0.6 V.

Supplementary Results



Figure S1 a) Mo 3d and b) S 2p XPS spectra of films prepared by annealing the (NH₄)₂MoS₄ precursor film at 200 °C (Film 1) and 420 °C (Film 2).

Supplementary Note to Figure S1: The Mo 3d states of MoS₃ (**Figure S1a**) shows two major peaks at 232.7 and 229.6 eV, attributed to Mo $3d_{3/2}$ and Mo $3d_{5/2}$ binding energies for Mo^V and Mo ^{IV}species for MoS₃ and MoS₂, respectively. A small amount Mo^{VI} is also presented, which should be attributed to the oxide impurity phase MoS_xO_y generated during the preparation process. The S 2p states of MoS₃ (**Figure S1b**) consists of two doublets peaks, which are assigned to divalent sulfide ions (S^{2–}) and single-valent sulfide ions (S₂^{2–}), respectively. The the fitted S^{2–}/S₂^{2–} peak area ratio is near 2. Quantification by XPS gave a Mo/S ratio of 1: 2.92 for Film **1** and 1:2.05 for Film **2**.



Figure S2 Histogram of device performance measured with 50 separately fabricated devices with and without HTL, the corresponding standard efficiency deviations are 0.06 and 0.16.



Figure S3 $(ahv)^2$ versus hv of Sb₂Se₃ film and MoS₃ film.



Figure S4 a) The efficiency degradation of devices with MoS₃ and Spiro-OMeTAD HTLs. The device parameters V_{OC} (b), J_{SC} (c) and FF (d) change over time (one week at 70 ± 10 °C, 70 ± 10% relative humidity).

Concentration (mg/mL)	Thickness (nm)	V _{OC} (mV)	J_{SC} (mA·cm ⁻²)	FF (%)	PCE (%)
0	0	329 ± 5.6	27.2 ± 1.24	45.1 ± 3.21	4.1 ± 0.58
10	12	361 ± 2.4	29.4 ± 0.54	58.0 ± 1.19	6.1 ± 0.29
20	30	379 ± 4.1	29.3 ± 0.57	61.5 ± 0.58	6.7 ± 0.15
25	47	361 ± 2.5	28.5 ± 0.91	60.5 ± 1.27	6.2 ± 0.23
30	65	354 ± 1.8	28.4 ± 0.53	54.9 ± 0.93	5.5 ± 0. 17

Table S1 Effect of $(NH_4)_2MoS_4$ precursor concentration on the device photovoltaic performance. (The annealing temperature in each film fabrication is 150 °C, the effective area of the device is 0.12 cm²)

Table S2 Statistics of device performance parameters of the best cell and average parameters (with standard deviation) of the Sb_2Se_3 solar cells based on MoS₃ films with different annealing temperatures. Thirty devices of each type were analyzed for the statistics. In all the device parameters with different fabrications, the first and second rows indicate the best and average parameters, the effective area of the device is 0.12 cm².

	V _{OC}	J _{SC}	FF	PCE	R _s	R _{SH}
	(mV)	(mA·cm ⁻²)	(%)	(%)	$(\Omega \cdot cm^2)$	(Ω·cm²)
W/O HTL	336	25.1	49.9	4.22	4.1	114.6
	337 ± 9	25.0 ± 0.4	46.1 ± 4.2	3.89 ± 0.30	5.3 ± 1.3	78.8 ± 22.7
150 °C	372	30.4	60.0	6.78	2.8	204.8
	371 ± 11	29.0 ± 0.7	60.7 ± 0.9	6.65 ± 0.10	3.3 ± 0.5	233.3 ± 79.8
200 °C	381	29.5	61.1	6.86	2.9	163.8
	380 ± 6	29.6 ± 0.6	60.8 ± 0.7	6.84 ± 0.07	2.96 ± 0.5	188.7 ± 71.4
250 °C	306	21.0	36.2	2.33	8.3	38.6
	312 ± 12	19.7 ± 1.5	32.6 ± 2.7	2.00 ± 0.22	11.7 ± 3.2	32.4 ± 6.9
300 °C	227	12.7	32.8	0.94	11.4	33.0
	203 ± 35	14.0 ± 1.7	30.1 ± 2.5	0.84 ± 0.11	11.2 ± 3.1	21.4 ± 8.2

Method	Device structure	V _{OC}	J_{SC}	FF	PCE	Ref
		$(\mathbf{m}\mathbf{v})$	(mA·cm ²)	(%)	(%)	
TE	ITO/CdS/Sb ₂ Se ₃ /Au	380	26.3	57	5.76	1
TE	FTO/CdS/Sb ₂ Se ₃ /Spiro/Au	361	31.7	56.9	6.50	2
TE	FTO/CdS/Sb ₂ Se ₃ /MoS ₃ /Au	381	29.5	61.1	6.86	this work
VTD	FTO/CdS/Sb ₂ Se ₃ /Au	420	29.9	60.4	7.6	3
VTD	ITO/CdS/Sb ₂ Se ₃ /CuSCN/Au	423	30.8	57	7.5	4

Table S3 Summary of reported Sb_2Se_3 solar cells on a superstrate structure. (TE: thermal evaporation; VTD: vapor transport deposition and Spiro: Spiro-OMeTAD)

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