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Aqueous solution processed MoS₃ as an eco-friendly hole-transport layer for all-inorganic Sb₂Se₃ solar cells[†]

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Here we report a solution processed environmentally friendly MoS_3 hole-transport material for Sb_2Se_3 solar cells, where MoS_3 exhibits a matched energy level relative to Sb_2Se_3 . In the synthesis, H_2S produced by the thermal decomposition of $(NH_4)_2MoS_4$ is found to efficiently eliminate the antimony oxide impurity formed on the Sb_2Se_3 surface. Finally, the all-inorganic Sb_2Se_3 solar cell delivers an efficiency of 6.86% with excellent stability.

Antimony selenide, Sb₂Se₃, has attracted great attention in solar cell applications due to its suitable optical band gap, abundant elemental reserves and excellent stability.^{1,2} Recent years have witnessed a dramatic increase in the efficiency of antimony chalcogenide-based devices. Most recently, both Sb₂Se₃ and alloy-type Sb₂(S,Se)₃ solar cells have achieved around 10% power conversion efficiency (PCE).^{1,3} Great efforts have been devoted to the fabrication of high-quality Sb₂Se₃ thin films, an emerging solar material. In principle, to further improve the performance of Sb₂Se₃ based solar devices, exploration of efficient and stable functional layers has to be considered. Furthermore, in terms of practical applications, it is desirable to develop more environmentally friendly functional layer materials along with convenient material processing.

The introduction of hole-transport layers (HTLs) to construct n-i-p structures is an important strategy to improve the hole extraction and transport in solar cells. Inspired by the development of perovskite and organic solar cells, organic hole-transport materials have been widely applied in Sb₂Se₃ solar cells, such as Spiro-OMeTAD,⁴ CZ-TA⁵ and PCDTBT.⁶ However, organic hole-transport materials often suffer from low hole

mobility and poor device stability.⁷ To date, however, limited work has been reported on well-matched inorganic holetransport materials for Sb₂Se₃-based solar cells. Solution processed hole-transport materials, PbS quantum dots⁸ and CuSCN⁹ have been applied in Sb₂Se₃ solar cells. The high efficiencies achieved with inorganic HTL based Sb₂Se₃ devices are around 7%. However, it is noted that HTLs involving toxic Pb are usually considered as potential problems in practical applications and the voltage-induced interfacial degradation observed between the CuSCN/Au layers would result in device efficiency degradation.¹⁰ Recently, the Mai group used trigonal selenium layers deposited by vacuum evaporation to construct an n-i-p FTO/SnO₂/CdS/Sb₂Se₃/Se/Au device structure,¹¹ where selenium was found to suppress the interfacial recombination.

In this work, we develop an eco-friendly hole-transport material MoS₃ to build n–i–p structured Sb₂Se₃ solar cells. The MoS₃ layer was prepared through spin-coating and subsequent thermal decomposition of aqueous $(NH_4)_2MoS_4$ solution. Besides the formation of the MoS₃ film, the thermal decomposition process also generates H₂S that reacts with Sb₂O₃ impurities, converting it to antimony chalcogenide so that the interfacial properties between the absorber and the hole-transport layers are improved. As a result, the extraction and collection of carriers are significantly improved, leading to remarkably enhanced short-circuit current density (I_{SC}) and fill factor (FF), which help these cells achieve a high efficiency of 6.86%. Concomitantly, our study shows that MoS₃ displays extraordinarily improved stability compared with conventional organic hole-transport materials.

MoS₃ thin films were prepared by the thermal decomposition of $(NH_4)_2MoS_4$ in an N₂ atmosphere. The detailed thermal decomposition process was studied *via* thermogravimetric analysis (TGA) performed in the range of 30–550 °C (Fig. 1a), where two thermal decomposition stages are observed. The first decomposition stage occurs at 140–200 °C, which leads to a weight loss of 34% at 200 °C and the product at this annealing temperature is MoS₃ (reaction (1)). At a temperature above





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Fig. 1 (a) TGA profile of $(NH_4)_2MOS_4$ in the range of 50-550 °C. (b) XRD patterns of MOS_3 deposited at different annealing temperatures. Surface SEM image and 3D AFM image of the Sb₂Se₃ films (c) without and (d) with the MOS_3 HTL.

350 °C, MoS_3 is further decomposed to form MoS_2 (reaction (2)), which induces further weight loss of 16%. This result is consistent with the literature report.¹² X-ray diffraction (XRD) characterization was done for the (NH₄)₂MoS₄ precursor films deposited on the silicon substrate annealing at 150-300 °C. The XRD patterns in Fig. 1b present a broad peak centered at 14° , which is the typical diffraction peak of amorphous MoS₃ and MoS₂. Further identification was performed via XPS spectra (Fig. S1, ESI[†]) for two samples which were prepared by annealing (NH₄)₂MoS₄ precursor films at 200 °C (film 1) and 420 °C (film 2). The S 2p XPS spectra of film 2 display only one S $2p_{3/2}$ peak at 162.5 eV, while that of film 1 show two S $2p_{3/2}$ peaks at 162.2 and 163.4 eV, well attributed to S^{2-} and S^{2-}_{2-} , respectively. Moreover, the fitted S^{2-}/S_2^{2-} peak ratio of film 1 was close to 2, agreeing well with the reported amorphous MoS₃.¹³ We thus propose that reaction (1) leads to the formation of MoS_3 at 200 °C.

$$(\mathrm{NH}_4)_2\mathrm{MoS}_4 \to \mathrm{MoS}_3 + \mathrm{H}_2\mathrm{S} + 2\mathrm{NH}_3 \tag{1}$$

$$MoS_3 \rightarrow MoS_2 + \frac{1}{2}S_2$$
 (2)

The Sb₂Se₃ thin film was deposited on the CdS-coated FTO (fluorine-doped tin oxide) substrate *via* a thermal evaporation approach and the MoS₃ film was deposited on the Sb₂Se₃ layer by spin-coating the (NH₄)₂MoS₄ precursor with a concentration of 20 mg mL⁻¹ (the detailed fabrication process and the effect of (NH₄)₂MoS₄ precursor concentration on the device photovoltaic performance are provided in the Experimental Section and Table S1 in ESI,† respectively). As a result, Sb₂Se₃ displays a uniform surface morphology with clear grain boundaries (Fig. 1c). Atomic force microscopy (AFM) measurement shows a surface roughness of 39.3 nm. Deposition of MoS₃ could evenly cover the Sb₂Se₃ surface, as shown in Fig. 1d. The film

surface becomes markedly flat and the average roughness decreased to 18.0 nm. The uniform surface coverage and the low surface roughness are desirable for the interfacial contract with the back electrode.

In order to explore the effect of the annealing temperature on the performance of the hole-transport layer, devices with the FTO/CdS/Sb₂Se₃/MoS₃/Au structure were fabricated (Fig. 2a). The thicknesses of the CdS buffer layer, Sb₂Se₃ absorber layer and MoS₃ layer were measured to be 60, 400, 30 nm, respectively (Fig. 2b). Fig. 2c presents the J-V curves of the bestperforming Sb₂Se₃ solar cells based on MoS₃ films with different annealing temperatures, which were measured under one Sun illumination (100 mW cm^{-2}). The detailed device parameters are listed in Table S2 (ESI[†]). Specifically, in the absence of hole-transport layer, the devices exhibit an average PCE of 3.89%. With the MoS₃ HTL annealed at 150 °C, the average PCE increased to 6.65%. All the photovoltaic parameters are essentially enhanced when compared with the device without a HTL, indicating the effectiveness of MoS₃ in hole extraction and transport. The efficiency of the device increased slightly with the annealing temperature in the range of 150-200 °C. The best photovoltaic parameters (J_{SC} = 29.5 mA cm², V_{OC} = 381 mV, FF = 61.1% and PCE = 6.86%) were achieved when the annealing temperature was 200 °C. Further increasing the annealing temperature over 200 °C leads to a gradually decreased device performance, and the PCE decreased to as low as 0.94% when annealing at 300 °C. The decrease in the device performance is most likely due to the interface diffusion between the Sb₂Se₃ and MoS₃ layers at a high annealing temperature, which will introduce defects that bring forth carrier recombination. We conducted further device investigations with the optimized fabrication conditions. The histogram of the device performance measured on 50 separately prepared devices with and without HTLs is shown in Fig. S2 (ESI[†]). The average efficiency of the devices without HTLs is 3.98%, while that of the devices with optimal HTLs is 6.70%, along with a reduced standard deviation. This result demonstrates that the MoS₃ HTL could



Fig. 2 (a) Schematic illustration of the device structure of an Sb₂Se₃ solar cell with MoS₃ as the HTL. (b) Cross-sectional SEM image of an Sb₂Se₃ solar cell with the MoS₃ HTL. (c) Current–voltage (*J*–*V*) curves of devices measured under simulated AM 1.5 illumination with MoS₃ HTLs annealing at different temperatures. (d) UPS spectra of the Sb₂Se₃ film. (e) UPS spectra of the MoS₃ film (annealing at 200 °C). (f) Band diagram of the CdS/Sb₂Se₃/MoS₃ structure.

significantly increase the device efficiency and reproducibility. It is noted that the device reported in this work achieves top efficiency for planar Sb₂Se₃ solar cells prepared by thermal evaporation (see Table S3, ESI† for the list of the state-of-thearts Sb₂Se₃ based devices with n–p and n–i–p structure).

To investigate the energy level arrangement between absorber layer Sb₂Se₃ and HTL MoS₃, we applied ultraviolet photoelectron spectroscopy (UPS) to measure the conduction band minimum (CBM), valence band maximum (VBM) and Fermi level $(E_{\rm F})$ of Sb₂Se₃ and MoS₃ films (Fig. 2d and e). Combined with the band gaps estimated from the ultraviolet-visible (UV-Vis) absorption spectra of Sb₂Se₃ and MoS₃ (Fig. S3, ESI[†]), the Fermi level, VBM, and CBM of Sb_2Se_3 are determined to be -4.50 eV, -5.08 eV, and -3.85 eV, respectively, while those of MoS₃ are -4.15 eV, -4.95 eV, and -2.95 eV. The proposed band diagram of CdS/Sb₂Se₃/MoS₃ is accordingly presented in Fig. 2f, which suggests that the dissociated electrons in Sb₂Se₃ could be blocked by the MoS₃ layer because of the large CBM offset of MoS₃, while the dissociated holes could be effectively extracted and transported to the MoS₃ layer. Therefore, MoS₃ is a suitable hole-transport material to form n-i-p structured Sb₂Se₃ solar cells.

It has been studied that Sb₂Se₃ films fabricated by physical deposition show Sb₂O₃ on the surface, which is considered as a detrimental impurity in solar cells that induces charge recombination.⁶ This is also true with our deposited Sb₂Se₃ film, where the binding energies at 538.5 and 540.0 eV by XPS characterization are ascribed to Sb 3d_{3/2} of Sb₂Se₃ and Sb₂O₃,¹⁴ respectively (Fig. 3a). Surface treatment with hydrochloric acid solution¹⁵ and (NH₄)₂S¹⁶ has preliminarily demonstrated the ability to remove the surface oxide impurities, while the treatments are accompanied by corrosion of the Sb₂Se₃ layer. For the (NH₄)₂MoS₄ precursor solution, it shows weak acidity due to the hydrolysis of NH4⁺ ions that could alleviate the surface damage. Furthermore, the thermal decomposition generated H₂S could react with Sb₂O₃ to form antimony sulfide. As shown in Fig. 3a, with the (NH₄)₂MoS₄ precursor solution spin-coated on it, the Sb₂Se₃ film (ii-Sb₂Se₃) shows a significantly reduced peak intensity of Sb₂O₃ compared with the as prepared Sb₂Se₃ film (i-Sb₂Se₃), while the Sb₂Se₃ film with an annealed MoS_3 film (iii-Sb₂Se₃) shows no obvious peaks at 540.0 eV, indicating the effective removal of Sb₂O₃ in the M-Sb₂Se₃ film.



Fig. 3 (a) XPS spectra of Sb 3d and (b) the Raman spectra of different Sb₂Se₃ films (i-Sb₂Se₃: the as prepared film by thermal evaporation; ii-Sb₂Se₃: the Sb₂Se₃ film with $(NH_4)_2MOS_4$ precursor spin-coating; iii-Sb₂Se₃: the Sb₂Se₃ film with annealed MoS₃).

In fact, XPS can only detect the surface composition, and the signal of Sb_2O_3 may also be covered by the post-deposited MoS_3 , instead of transforming to sulfide as described above. To draw a clear conclusion, we conducted Raman scattering characterization (Fig. 3b). The two main bands (190 cm⁻¹ and 210 cm⁻¹) matched well with the orthorhombic Sb_2Se_3 phase for the three Sb_2Se_3 films.¹⁵ However, the i-Sb_2Se_3 film showed an obvious Sb_2O_3 peak at 253 cm⁻¹,¹⁷ while the peak intensity at 253 cm⁻¹ was very weak in the ii-Sb_2Se_3 film. For the iii-Sb_2Se_3 film, the Sb_2O_3 peak at 250 cm⁻¹ disappeared completely, accompanied by the appearance of new peaks at 377 and 403 cm⁻¹ for MoS_3 .¹⁸ The result indicates that the fabrication process has a desirable effect on the removal of Sb_2O_3 .

The introduction of the MoS₃ hole-transport layer is expected to improve the photoexcited carrier collection. Therefore, external quantum efficiency (EQE) spectra (Fig. 4a) were recorded to investigate the photo-response of the devices with and without HTLs. As the CdS electron transport layer and the interface between the CdS and Sb₂Se₃ layers are the same, the transport process for the photo-excited carriers near the CdS-Sb₂Se₃ heterojunction is almost unaffected. As a result, the improvement of quantum efficiency at short wavelengths (<550 nm) is insignificant. At longer wavelengths (550-1000 nm), the EQE spectra show a noticeable improved photoresponse for the device with an MoS₃ HTL. This indicates that the photogenerated holes could transport through Sb₂Se₃ with a significantly reduced recombination, suggesting that the introduction of the MoS₃ HTL can effectively extract the holes and thus reduce the charge recombination.

To further explore the mechanism by which the V_{OC} and FF are enhanced, Mott–Schottky ($C^{-2}-V$) and electrochemical impedance spectroscopy (EIS) measurements in the dark were performed. The $V_{\rm bi}$ value is the point at which the linear part of the $C^{-2}-V$ curve is extrapolated to the *X*-axis. As seen from Fig. 4b, the $V_{\rm bi}$ values for the device without an HTL and the device with an MoS₃ layer are 367 mV and 430 mV, respectively.



Fig. 4 (a) External quantum efficiency (EQE), (b) Mott–Schottky ($C^{-2}-V$) characteristics, (c and d) Nyquist plots in the dark at 0.3 V of the device without an HTL and with an MoS₃ HTL.

 $V_{\rm bi}$ is closely related to the $V_{\rm OC}$ of the devices, so the slight increase in $V_{\rm OC}$ is due to an increase in the device $V_{\rm bi}$. The benign Sb₂Se₃/MoS₃ junction interface with favorable energy level alignment reduces the Schottky barrier at the back contact, leading to a positive effect on the main p-n junction. Moreover, a wider depletion width W_d was calculated from the Mott–Schottky ($C^{-2}-V$) measurements for the device with an MoS₃ layer (device without HTL: 227 nm; device with MoS₃:248 nm). The wider W_d could facilitate carrier generation in the p-n junction and hole extraction to the HTL with a reduced probability of being trapped and recombined during the transport process.

The EIS curve of the device without an HTL is well fitted with two shunt circuits (Fig. 4c and d), while that of the device with an MoS₃ HTL could be fitted with one shunt circuit. The recombination resistance R_2 (1349 Ω cm²) for the device with an MoS₃ HTL is much larger than either of the recombination resistances R_2 (330 Ω cm²) and R_3 (235 Ω cm²) for the device without an HTL. As discussed above, the device with an MoS₃ HTL would form a benign interface between Sb₂Se₃/MoS₃ upon the effective removal of Sb₂O₃. The optimized interface could result in a reduction of carrier recombination for the improvement of FF.

Finally, MoS₃ as an inorganic hole-transport material also effectively improves the stability of the device. As shown in Fig. S4a (ESI[†]), the efficiency of the unencapsulated device with an MoS3 HTL was maintained in an ambient environment for up to six months. Further tests under extreme conditions $(70 \pm 10 \,^{\circ}\text{C}, \, 70\% \pm 10\%$ relative humidity, in the dark) for the same device were carried out for one week. More than 85% of the initial efficiency of 6.78% was maintained after 160 hours for the device with an MoS₃ HTL. However, Spiro-OMeTAD, an organic hole-transport layer material in Sb₂Se₃ solar cells, exhibited poor humidity and temperature stability. The device with the Spiro-OMeTAD HTL showed a 60% efficiency decrease after 160 hours. The degradation behavior of the device parameters (V_{OC} , J_{SC} and FF) is shown in Fig. S4b-d (ESI⁺). Clearly, there are significant decreases in all the three parameters in the Spiro-OMeTAD HTL based device under these extreme conditions when compared with the device based on the MoS₃ HTL. The Spiro-OMeTAD doped with lithium salt is easy to be oxidised in air. This characteristic impairs the hole-transport ability and the device performance.

In summary, we have demonstrated that MoS_3 could be applied as an efficient hole-transport layer in Sb_2Se_3 solar cells, and the corresponding power conversion efficiency reached 6.86%, which is compared with those in solar cells of this material using the best performing organic hole conductor Spiro-OMeTAD. MoS_3 is an eco-friendly hole-transport material, and the aqueous solution process is facile and of low-cost. During material processing, we found that Sb_2O_3 on the surface This work was supported by the National Natural Science Foundation of China (U19A2092 and U1732150) and the National Key Research and Development Program of China (2019YFA0405600).

Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

- 1 Z. Li, X. Liang, G. Li, H. Liu, H. Zhang, J. Guo, J. Chen, K. Shen, X. San, W. Yu, R. E. I. Schropp and Y. Mai, *Nat. Commun.*, 2019, 10, 125.
- 2 X. Wen, C. Chen, S. Lu, K. Li, R. Kondrotas, Y. Zhao, W. Chen, L. Gao, C. Wang, J. Zhang, G. Niu and J. Tang, *Nat. Commun.*, 2018, 9, 2179.
- 3 R. Tang, X. Wang, W. Lian, J. Huang, Q. Wei, M. Huang, Y. Yin, C. Jiang, S. Yang, G. Xing, S. Chen, C. Zhu, X. Hao, M. A. Green and T. Chen, *Nat. Energy*, 2020, 5, 587–595.
- 4 Y. Ma, B. Tang, W. Lian, C. Wu, X. Wang, H. Ju, C. Zhu, F. Fan and T. Chen, J. Mater. Chem. A, 2020, 8, 6510–6516.
- 5 D.-B. Li, X. Yin, C. R. Grice, L. Guan, Z. Song, C. Wang, C. Chen, K. Li, A. J. Cimaroli, R. A. Awni, D. Zhao, H. Song, W. Tang, Y. Yan and J. Tang, *Nano Energy*, 2018, **49**, 346–353.
- 6 Y. C. Choi, T. N. Mandal, W. S. Yang, Y. H. Lee, S. H. Im, J. H. Noh and S. I. Seok, *Angew. Chem., Int. Ed.*, 2014, **53**, 1329–1333.
- 7 X. Qin, Z. Zhao, Y. Wang, J. Wu, Q. Jiang and J. You, J. Semicond., 2017, 38, 011002.
- 8 C. Chen, L. Wang, L. Gao, D. Nam, D. Li, K. Li, Y. Zhao, C. Ge, H. Cheong, H. Liu, H. Song and J. Tang, ACS Energy Lett., 2017, 2, 2125–2132.
- 9 K. Li, S. Wang, C. Chen, R. Kondrotas, M. Hu, S. Lu, C. Wang, W. Chen and J. Tang, J. Mater. Chem. A, 2019, 7, 9665–9672.
- 10 N. Arora, M. I. Dar, A. Hinderhofer, N. Pellet, F. Schreiber, S. M. Zakeeruddin and M. Grätzel, *Science*, 2017, 358, 768–771.
- 11 K. Shen, Y. Zhang, X. Wang, C. Ou, F. Guo, H. Zhu, C. Liu, Y. Gao, R. E. I. Schropp, Z. Li, X. Liu and Y. Mai, *Adv. Sci.*, 2020, 2001013.
- 12 A. J. Jacobson, R. R. Chianelli, S. M. Rich and M. S. Whittingham, *Mater. Res. Bull.*, 1979, **14**, 1437–1448.
- 13 K. S. Liang, S. P. Cramer, D. C. Johnston, C. H. Chang, A. J. Jacobson, J. P. deNeufville and R. R. Chianelli, *J. Non-Cryst. Solids*, 1980, 42, 345–356.
- 14 Y. Yin, C. Wu, R. Tang, C. Jiang, G. Jiang, W. Liu, T. Chen and C. Zhu, *Sci. Bull.*, 2019, **64**, 136–141.
- 15 C. Wang, S. Lu, S. Li, S. Wang, X. Lin, J. Zhang, R. Kondrotas, K. Li, C. Chen and J. Tang, *Nano Energy*, 2020, **71**, 104577.
- 16 C. Chen, Y. Zhao, S. Lu, K. Li, Y. Li, W. Chen, L. Wang, D. Li, H. Deng, F. Yi and J. Tang, *Adv. Energy Mater.*, 2017, 7, 1700866.
- 17 A. Shongalova, M. R. Correia, B. Vermang, J. M. V. Cunha, P. M. P. Salomé and P. A. Fernandes, *MRS Commun.*, 2018, 8, 865–870.
- 18 X. Li, W. Zhang, Y. Wu, C. Min and J. Fang, ACS Appl. Mater. Interfaces, 2013, 5, 8823–8827.