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Engineering of the perovskite/electron-transporting layer interface with transition metal chalcogenides for improving the performance of inverted perovskite solar cells†

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Layered two-dimensional (2D) transition-metal chalcogenides (TMCs) attract substantial interest across multiple disciplines due to their unique properties. In perovskite solar cells (PSCs), researchers have extensively explored the integration of 2D TMCs to enhance device power conversion efficiency (PCE) and stability. However, there is a research gap in understanding their impact on inverted (p–i–n) PSCs, especially at the perovskite/electron-transporting layer (ETL) interface. This study addresses this gap by investigating the effect of inserting InSe, $MoSe_2$, and SnS_2 nanosheets at the perovskite/ETL interface in inverted PSCs. The introduction of 2D TMC interlayers induces a downward shift in perovskite energy levels, optimizing the energy level alignment at the perovskite/ETL interface and substantially increasing the PCE. The SnS_2-incorporating PSCs exhibit the highest relative improvement of 5.05% (InSe and $MoSe_2$ nanosheets yield 3.37% and 2.5% PCE increase, respectively). This enhancement results in an absolute PCE of 18.5% with a fill factor exceeding 82%. Furthermore, the incorporation of InSe nanosheets eliminates the burn-in phase enhancing the long-term stability (T_{70} of 250 h) of unencapsulated devices. This study underscores the significant improvement in PSCs' PCE and stability by selectively incorporating suitable TMCs at the perovskite/ETL interface. This research offers insights into the potential role of TMCs in advancing PSCs.

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Introduction

Transition metal chalcogenides (TMCs) represent a highly promising class of materials with a wide range of applications. These materials exhibit exceptional optical, electrical, catalytic, and mechanical properties, making them suitable for numerous fields, including batteries,[1,2] supercapacitors,[3], (photo)catalysis,[4–8], (photo)transistors[9–11] and other optoelectronic devices.[12–17] One feature of TMCs is their band gap tunability, which makes them ideal for adjustable light absorption, *e.g.*, serving as the photoactive layer in photovoltaic applications. However, photovoltaic devices using TMC-based photoactive layers currently exhibit insufficient power conversion efficiency (PCE) just above 5%.[18,19] When integrated with other photoactive layers as interlayers or additives, TMCs have been reported to enhance the performance of solar cells by finely tuning specific device characteristics, ultimately improving the overall performance.[20] For instance, MoS_2 has been successfully integrated into both Si-based[21,22] and organic solar cells,[23] improving significantly the cell performance. The role of TMCs depends specifically on photovoltaic technologies, for each of which a systematic investigation of the role of TMCs is required for reliable advancements in this field.[24]

In this context, the incorporation of TMCs, typically in their two-dimensional (2D) forms (*i.e.*, nanosheets), in perovskite solar cells (PSCs) has been investigated in various studies.[24–26] In particular, MoS_2 was deposited on the perovskite in normal (n–i–

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† Electronic supplementary information (ESI) available: Material synthesis, exfoliation, and characterization, PSC fabrication and characterization. Moreover, in the supplementary material are presented the TEM statistical analysis, XPS spectra, SEM images, box charts of PSC photovoltaic parameters, W_F measurements, and APS measurements. See DOI: https://doi.org/10.1039/d4se00212a

p) PSCs, acting as an interlayer between the perovskite and the hole-transporting layer (HTL) to enhance the device PCE and stability by improving the hole extraction processes and offering a physical barrier against ion migration from the metal contact to the perovskite and *vice versa*.[27–29] In a similar study, $MoSe_2$ nanosheets were also screened together with MoS_2 ones to form thin interlayers between the perovskite and the HTL in normal PSC structures, enhancing the performance of reference devices.[30–32] MoS_2 was also used in combination with graphene-incorporating electron transporting layers (ETLs) and MXene-incorporating perovskites, testifying the effectiveness of 2D material interface engineering.[33,34] Also, TMCs have been proposed as charge-transporting layers to completely replace conventional materials of PSCs.[24,35] Specifically, MoS_2 and WS_2 were used as HTLs in inverted PSCs showing similar PCEs to the references based on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS).[36,37] SnS_2 was used as the ETL in PSCs, improving the PCE up to 20%.[38] Despite its n-type behavior, $MoSe_2$ was used as an HTL in an inverted PSC,[39] showing a high PCE of 18%. The mixing of PEDOT:PSS with MoS_2, as well as other dichalcogenides, was used to increase the PCE of inverted PSCs.[40–42] Dichalcogenides, including MoS_2, but also other TMCs, have also been proposed to modify the electron-transporting layer (ETL)/metal electrode interface, aiming at creating favorable energy level alignments to efficiently collect photogenerated electrons.[26,43–45]

Despite the tremendous progress recently achieved by incorporating MoS_2 in PSCs, including the realization of the world's first perovskite solar farm operating for several months,[46] other representative TMCs for photovoltaic applications, based on the above consideration, are SnS_2, $MoSe_2$, as well as monochalcogenides, *e.g.*, InSe.[24] While MoS_2 is mainly used to improve the hole extraction efficiency in n–i–p PSCs, there are other TMCs that may play a relevant role in promoting the electron extraction from the perovskite to the current collectors. In particular, SnS_2 is an n-type layered semiconductor with a tunable band gap ranging from 2.1 to 3.4 eV, depending on the number of its layers. In its bulk form, SnS_2 has already been established in photovoltaic applications.[47] Meanwhile, the exfoliation of SnS_2 into 2D few-layer nanosheets has been achieved through both chemical[48] and physical methods.[49] Extensive characterization of SnS_2 has revealed that its monolayer possesses an indirect bandgap equal to 2.033 eV, while its field-effect transistor (FET) mobility was estimated to be in the range of 5 $cm^2\ V^{-1}\ s^{-1}$ to 250 $cm^2\ V^{-1}\ s^{-1}$,[50] enabling the realization of ultrathin FETs and logic gates.[49] Also, SnS_2 shows a high electron density of $\sim 6 \times 10^{-19}$ cm^{-3},[48] justifying its use as an effective dopant for $PC_{70}BM$ in inverted PSCs.[51] In this context, the high conductivity of 2D SnS_2 has been leveraged for the fabrication of ultra-thin ETLs in PSCs.[38,52] The valence band maximum (VB) and conduction band minimum (CB) of 2D SnS_2 have been estimated through ultraviolet photoelectron spectroscopy (UPS) to be −6.54 and −4.24 eV, respectively, indicating their potential ability to collect electrons from common perovskite active layers.[38]

$MoSe_2$ shows a similar structure to that of MoS_2 (2H phase). $MoSe_2$ is a semiconductor with an indirect band gap of 1.41 eV.[53] However, few-layer $MoSe_2$ exhibits a direct band gap of 1.58 eV (ref. 53 and 54) and a FET electron mobility of 50–250 $cm^2\ V^{-1}\ s^{-1}$.[55] Thin-films of 2D $MoSe_2$ have been used in photovoltaics,[56,57] catalysis for the hydrogen evolution reaction,[58,59] and energy storage systems.[60,61]

Finally, InSe is a III–VI layered compound made of stacked quaternary layers of Se–In–In–Se atoms that are held together by van der Waals interactions. Consequently, bulk InSe can be exfoliated into 2D forms by means of various methods, including scalable liquid-phase exfoliation (LPE) techniques.[62–64] InSe is generally considered as an n-type semiconductor and it was shown through experimental and theoretical studies that a band gap transition from direct to indirect occurs when InSe layer thickness reduces below 6 nm.[65] Also, its bandgap can increase from ∼1.2 eV for the bulk to 1.4 eV for few-layers InSe[66] and up to 2.1 eV for a monolayer of InSe.[67] The electron affinity was found to be −4.55 eV and the work function (W_F) to be 5.1 eV for bulk InSe.[68] The Hall mobility of InSe nanosheets was estimated to be $\sim 10^3$ $cm^2\ V^{-1}\ s^{-1}$ at room temperature (RT)[69] and the carrier density was measured to be $\sim 10^{13}$ cm^{-2}.[70] Pioneering studies also demonstrated n-type FETs based on 2D InSe, with an electron mobility at room temperature (RT) on the order of 10^3 $cm^2\ V^{-1}\ s^{-1}$.[71] This electron mobility is higher than those achieved by other high mobility 2D semiconducting materials, including MoS_2. Based on its properties, 2D InSe has been used in photovoltaic devices,[72,73] as well as for (photo)electrochemical water splitting reactions,[64] photodetectors,[63,74] sensors,[75] thermoelectric devices,[76] and spintronic devices.[77]

Overall, the above discussed TMCs represent interesting 2D materials for the engineering of the perovskite/ETL interface, aiming at improving the device PCE. Most studies on incorporating TMCs in PSCs have been focused on the optimization of the perovskite/HTL interface. To the best of our knowledge, there is no systematic work on engineering the perovskite/ETL interface with TMCs. In this study, we aim to fill this research gap by studying representative TMCs, *i.e.*, SnS_2, $MoSe_2$ and InSe, to optimize the perovskite/ETL interface in inverted PSCs. Selected TMCs, exfoliated through LPE, were deposited over the perovskite layer using solution processing, ensuring the scalability and industrialization feasibility of our interface engineering approach. The insertion of TMCs between the perovskite layer and the $PC_{70}BM$ effectively aligns the energy levels of the materials, enabling an efficient electron extraction from the perovskite to the current collector. This research aims to contribute to the extension of current 2D material interface engineering strategies to PSCs, providing new insights into the application of TMCs in inverted PSCs. The findings of this study have implications on the development of high-performance solar cells and can boost the utilization of TMCs in large-scale solar energy production, as already demonstrated for 2D MoS_2.[46]

Results

The methods of bulk TMC synthesis and exfoliation, and those for characterization of the exfoliated TMCs, are reported in the

ESI.† In particular, bulk 2H-$MoSe_2$, 2H-SnS_2 and β-InSe were exfoliated through ultrasonication-assisted LPE in isopropyl alcohol (IPA),[78,79] followed by sedimentation-based separation (SBS) to remove unexfoliated crystals from the exfoliated material.[59,80] Fig. 1a, d and g show the transmission electron microscopy (TEM) images of representative nanosheets of $MoSe_2$, SnS_2 and InSe, respectively. Fig. S1† reports the statistical analysis of the lateral size of the nanosheets. The lateral size data approximately follow log-normal distributions, with modes of 52.9 nm, 99.1 nm, and 143.9 nm for $MoSe_2$, SnS_2 and InSe nanosheets, respectively. Fig. 1b, e and h report the XRD patterns recorded for $MoSe_2$, SnS_2 and InSe nanosheets, respectively, comparing them with those measured for the bulk counterparts. The positions of the diffraction peaks of the exfoliated samples resemble those of the bulk counterparts, well-matching with the patterns of their hexagonal phases, *i.e.*, 2H-$MoSe_2$, $P\bar{6}m2$ space group, JCPDS card no. 029-0914; 2H-SnS_2, $P6_3mc$ space group, JCPDS card no. 023-0677; β-InSe structure, $P6_3/mmc$ space group, JCPDS card no. 034-1431. Bulk crystals show the diffraction peaks belonging to the {00l} family, which means that they are aligned along the (001) plane perpendicular to the *c* axis. Compared to the bulk materials, $MoSe_2$ and InSe nanosheets exhibit additional XRD peaks, likely due to their disordered arrangements. SnS_2 nanosheets, instead, preserve a placement perpendicular to their *c* axis. The broadening of the XRD peaks in the exfoliated materials indicate that their crystal sizes decreased after the LPE process. Fig. 1c, f and i report the Raman spectra of the bulk and exfoliated materials, exhibiting the characteristic Raman modes expected for each material by the group theory.[81–83] In $MoSe_2$ nanosheets, the redshift of the A_{1g} peak compared to the same peak of the bulk counterpart is explained by the softening of the

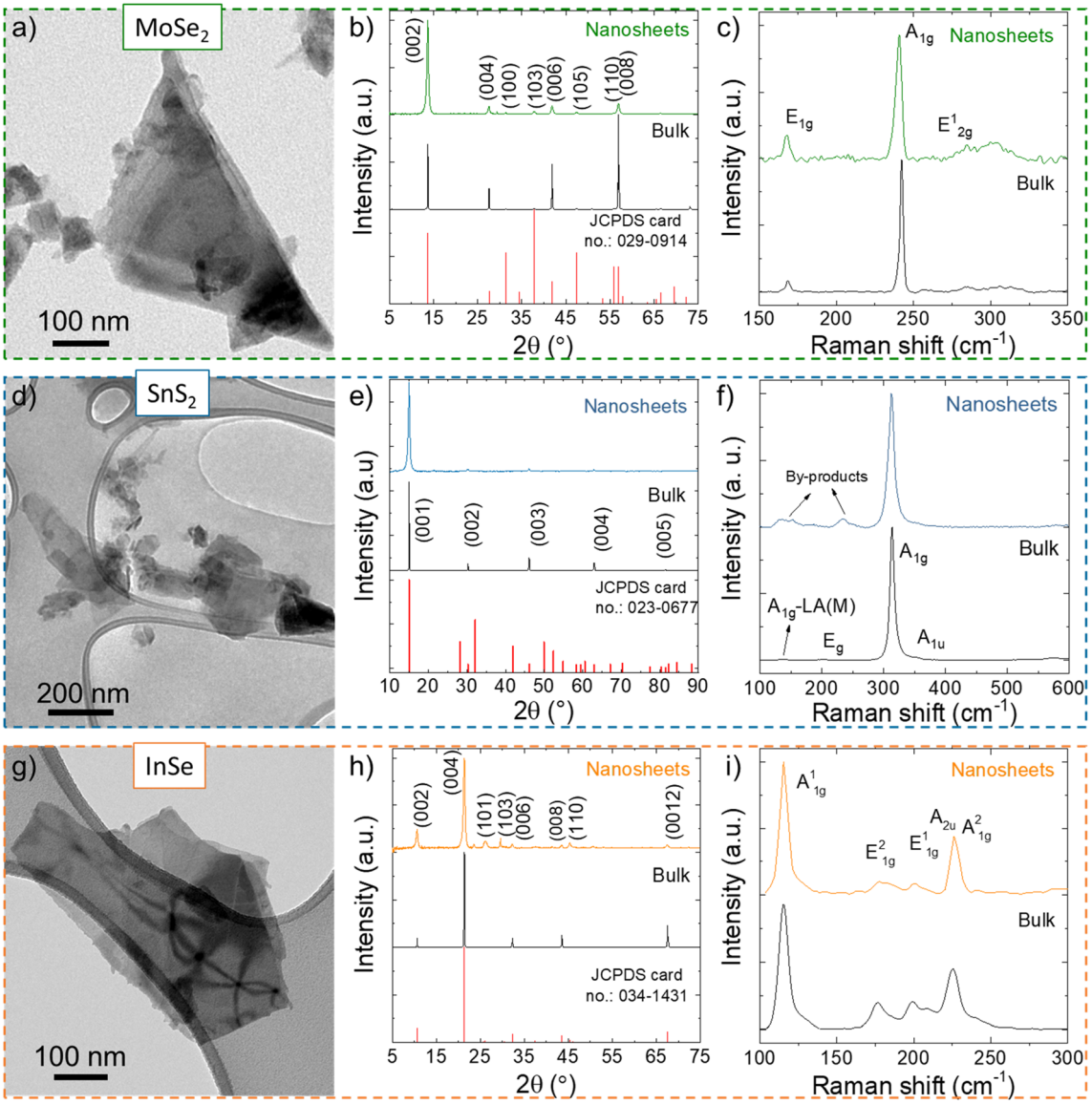

Fig. 1 TEM images, XRD patterns and Raman spectra measured for (a–c) $MoSe_2$, (d–f) SnS_2 and (g–i) InSe nanosheets. The XRD patterns and Raman spectra of bulk counterparts are also shown for comparison.

vibrational mode with decreasing the crystal thickness.[84,85] The Raman spectrum of bulk SnS_2 shows two phonon modes at ~313 cm^{-1} (A_{1g}) and ~203 cm^{-1} (E_g), as well as a weak two-phonon scattering signal of A_{1g}-LA (M) (Fig. 1f).[86] After exfoliation, additional peaks appear and are likely associated with by-products, *e.g.*, oxides.[87] Finally, bulk and exfoliated InSe exhibit various Raman peaks at similar positions, *i.e.*, A^1_{1g} at ~116 cm^{-1}, E^2_{1g} at ~177 cm^{-1}, E^1_{2g} at ~199 cm^{-1}, A_{2u} at ~208 cm^{-1}, and A^2_{1g} at ~227 cm^{-1}, which is consistent with previous studies.[63,64]

The deposition of TMC nanosheets was carried out by spin coating their dispersion (formulated in chlorobenzene) onto the perovskite layer. Successive spin coating steps were applied to optimize the interlayer of TMC nanosheets at the perovskite/$PC_{70}BM$ interface. The formation of ultrathin 2D TMC films on the surface of the perovskites was assessed through X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) measurements. As shown in Fig. S2,† the 3d In, Mo, and Sn XPS spectra, acquired on the perovskite surfaces treated with 2D TMCs, confirm the presence of InSe, $MoSe_2$ and SnS_2 nanosheets, respectively. Fig. S3† presents top-view SEM images of the perovskite surface treated with 2D TMCs. The images show scattered TMC nanosheets atop the perovskite surface, without the presence of large material aggregates. Importantly, the few-layer nature of the exfoliated TMCs permits nanometer-thick interlayers to be obtained without resulting in significant changes of the surface topography of the underlying perovskite film.

The effect of the 2D TMC interlayers between the perovskite and $PC_{70}BM$ layers was evaluated by measuring the device performance estimated through the analysis of their *J–V* curves under 1 sun illumination. Fig. S4–S6† report the statistical analysis of the photovoltaic parameters, *i.e.*, PCE, open circuit voltage (V_{oc}), fill factor (FF) and short circuit current (J_{sc}), for the investigated devices, produced with different 2D TMC interlayers and by varying the number of successive spin coating steps used for the deposition of 2D TMCs atop the perovskite. These data indicate that the number of spin coating steps has a significant impact on the final photovoltaic parameters of the devices. Specifically, exceeding two spin coating steps has a detrimental effect on the device performance. This negative effect is likely associated with the excessive exposure of the perovskite layer to the solvent of 2D TMC dispersions. Importantly, the incorporation of 2D TMCs into the device structure through one or two spin coating steps always increases the PCE of the device. In addition, different 2D TMC interlayers result in the improvement of specific photovoltaic parameters, indicating different beneficial effects of the investigated materials. To compare the devices that have different 2D TMC interlayers and to eliminate any uncontrollable effect between various fabrication batches, Fig. 2 plots the percentage relative change of PCE and of the other photovoltaic parameters measured for the most performing 2D TMC-incorporating PSCs compared to reference (without 2D TMCs) devices. Cells incorporating InSe and SnS_2 nanosheets exhibit a similar behavior, characterized by a substantial increase in their FF by 2.32% and 2.83%, respectively, along with a slight improvement in J_{sc}, and no change in V_{oc}, compared to the reference device. Differently, the

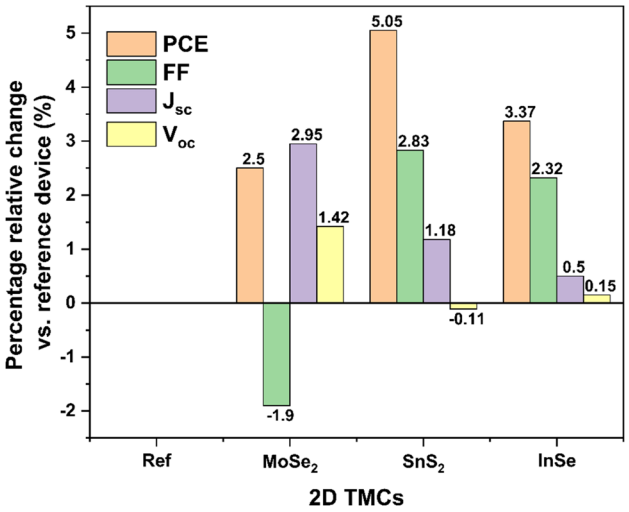

Fig. 2 Percentage relative change of PCE, FF, V_{oc}, and J_{sc} of 2D TMC-incorporating PSCs compared to reference (without 2D TMCs) PSCs.

device containing $MoSe_2$ nanosheets exhibits a decrease in FF by about 1.9% compared to the reference cell. Meanwhile the J_{sc} increases considerably by 2.95% and the V_{oc} increases by 1.42% compared to the reference cell. Notably, the devices incorporating SnS_2 nanosheets demonstrated the greatest relative PCE improvement of 5.05%, with a 2.83% increase in FF, resulting in a PCE as high as 18.5% and FF of 82%. Fig. S7† shows the external quantum efficiency spectrum of the best device.

The optoelectronic properties of the perovskite surface treated with 2D TMCs were investigated to assess if they are correlated with the device photovoltaic parameters. The W_F and valence band (VB) maximum energy of the perovskite surface were estimated using ambient photoemission spectroscopy measurements. Fig. S8† illustrates the W_F measurements of the perovskite surface before and after the deposition of 2D TMCs, and the extrapolated W_F values are listed in Table 1. The W_F of the pristine perovskite was determined to be 4.15 eV and increased after depositing the 2D TMCs (*i.e.*, 4.8 eV after SnS_2 nanosheet deposition). This behavior suggests the presence of a surface dipole that shifts the perovskite vacuum level to higher energies, with the negative part of the dipole facing outward from the surface (positive part facing toward the perovskite). The value of the interface dipole, Δ, for each case is listed in Table 1. Fig. S9† shows the VB measurements for the investigated samples. Interestingly, compared to the untreated

Table 1 Energy level values of the perovskite without 2D TMCs (reference) and the with 2D TMC interlayers at the perovskite/$PC_{70}BM$ interface. The CBO and VBO values are defined in the text and are calculated from eqn (1) and (2). Δ is the size of the interface dipole at the perovskite interface

Perovskite	W_F (eV)	Δ (eV)	VB (eV)	CB (eV)	CBO (eV)	VBO (eV)
Reference	−4.15		−5.41	−3.82	−0.08	−0.01
InSe	−4.46	0.31	−5.49	−3.9	0.00	−0.09
SnS2	−4.82	0.67	−5.47	−3.88	−0.02	−0.07
MoSe2	−4.73	0.58	−5.52	−3.93	0.03	−0.12

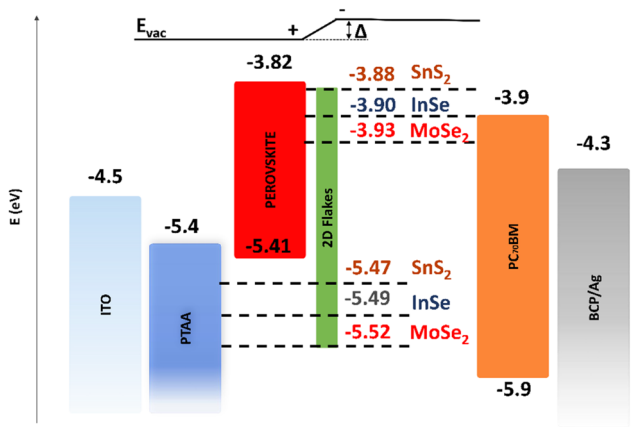

Fig. 3 Sketch of the energy level diagram of the investigated devices (energy values are not in scale). The dashed lines show the energy levels of the perovskite after the deposition of InSe, SnS_2, and $MoSe_2$ nanosheets.

perovskite, the presence of 2D TMCs shifts the perovskite VB to lower energy. Fig. 3 reports the sketch of the energy level diagram expected for the investigated cell configurations. The incorporation of 2D TMCs alters the energy level alignment at the interfaces between the perovskite and the $PC_{70}BM$. Specifically, the conduction band (CB) minimum energy and VB maximum energy shift to lower values. Thus, the CB minimum energy of the perovskite approaches that of $PC_{70}BM$, while the VB maximum energy of the perovskite moves away from that of PTAA. To quantify the offset of the energy levels, the energy difference between the CB minimum energies (conduction band offset-CBO) and the difference between the VB maximum energies (valence band offset-VBO) of the respective charge transporting layers and the perovskite were evaluated. In greater detail, the CBO and VBO can be calculated as:

$$\mathrm{CBO} = \chi_{\mathrm{perovskite}} - \chi_{\mathrm{PCBM}} \quad (1)$$

$$\mathrm{VBO} = \chi_{\mathrm{PTAA}} + E_{\mathrm{g,PTAA}} - (\chi_{\mathrm{perovskite}} + E_{\mathrm{g,perovskite}}) \quad (2)$$

in which χ is the electron affinity and E_g is the bandgap of the material indicated in the subscript.

The measured values for VB maximum energies and the calculated values for CBO and VBO are listed in Table 1. For the reference device, the CBO is negative (−0.08 eV), indicating that the CB minimum energy of $PC_{70}BM$ is lower than that of the perovskite. This energy level alignment at the perovskite/$PC_{70}BM$ interface is commonly indicated as a "cliff," signifying the absence of an energy barrier for electron injection from the perovskite to the $PC_{70}BM$. Similarly, the VBO for the reference device is −0.01 eV, implying no injection barrier for holes at the PTAA/perovskite interface. However, the CBO and VBO change drastically upon the deposition of 2D TMCs atop the perovskite. The CBO is reduced to −0.02 eV after the deposition of SnS_2 nanosheets and becomes 0.00 eV after depositing InSe nanosheets. Conversely, the CBO is positive (0.03 eV) when $MoSe_2$ nanosheets are deposited atop the perovskite, resulting in the formation of a "spike" feature at the perovskite/$PC_{70}BM$ interface.

In our previous work, we have demonstrated that the doping of the perovskite with BiTeI nanosheets leads to a modification of the energy levels of the perovskite.[88] In this context, increasing the CBO and decreasing the VBO have proven to be advantageous for device performance. Similar to our previous findings, tuning the CBO and VBO by incorporating TMC interlayers enhances the FF and, thus, the PCE of PSCs, as demonstrated for PSCs containing InSe and SnS_2 nanosheets. In the case of $MoSe_2$-containing PSCs, the formation of a "spike" level alignment at the interface is also expected to enhance the FF. However, a decrease in FF was observed together with an increase in V_{oc}, suggesting a different behavior of $MoSe_2$ nanosheets compared to SnS_2 and InSe nanosheets. The VBO of the reference sample (−0.01 eV) decreases to −0.12 eV with the incorporation of the $MoSe_2$ interlayer. Our previous work has demonstrated that lowering the VBO is advantageous for device performance, as it reduces non-radiative recombination at the interface between the HTL (PTAA) and the perovskite.[88] Moreover, experimental and theoretical studies have emphasized the importance of an absolute energy level offset of approximately 0.2 eV at the PTAA/perovskite interface.[89] Additionally, a VBO between 0 and −0.18 eV has been identified as the optimum range for efficient hole extraction.[90] Therefore, the observed improvement in V_{oc} for $MoSe_2$ can be attributed to the reduced recombination at the PTAA/perovskite interface, as the incorporation of $MoSe_2$ helps to tune the VBO closer to the theoretically optimum range. The improved PCE of devices incorporating InSe can be attributed to the tendency of this material to oxidize under ambient conditions, forming In_2O_3. Notably, the surface of InSe readily undergoes oxidation when subjected to air heat treatment.[91–93] The native oxide In_2O_3 is an n-type semiconductor with an optical band gap of 3.66 eV[92] and a high carrier concentration of approximately 6×10^{19} cm^{-3},[68,94] which can improve device PCE. Theoretical studies have indicated that H_2O, N_2, and O_2 molecules physisorbed onto the 2D InSe surface, resulting in partial electron charge transfer from InSe to the adsorbed molecules.[95] Additionally, it has been shown that a monolayer of InSe readily physisorbs H_2O under ambient conditions, irrespective of the presence of In or Se vacancies. Depending on the vacancies, InSe can be doped with H_2O, leading to either p-type (In vacancies) or n-type (Se vacancies) behavior,[96] suggesting precaution to assess the actual role of the InSe interlayers. The interface dipole at the interface of perovskite/ETL could reduce interface recombination, by preventing electron carriers in the ETL from reaching the interface.

The incorporation of 2D TMCs atop the perovskite has been the subject of extensive research, and our findings supplement previous studies, mainly focused on dichalcogenides and normal PSCs. Indeed, we have observed a strong agreement between our results and a theoretical study investigating the perovskite/InSe interface,[97] in which it was shown that InSe plays a crucial role in facilitating electron charge transport, causing charge transfer from the perovskite towards the InSe. In line with this, we have observed that the W_F of the perovskite surface covered with InSe nanosheets is higher than that of the control sample, indicating the accumulation of negative charge

on the top surface with InSe, forming an interface dipole, as well as for the other investigated 2D TMCs.[97] Furthermore, experimental evidence has shown that the interfaces of TMCs such as MoS_2, WSe_2, and $MoSe_2$ with inorganic perovskites exhibit ultrafast and efficient charge carrier transfer.[98,99] Based on these findings, it is expected that the presence of 2D TMCs on the perovskite will not impede charge transport, a hypothesis that is confirmed by our experimental results. Moreover, SnS_2 nanosheets have been utilized in the literature to form the ETL, enhancing charge extraction and passivating interfacial traps more efficiently compared to SnO_2.[38] Our results are aligned with this, further supporting the beneficial effects of SnS_2 as an ETL in PSCs. Consequently, our study provides additional insights on the incorporation of the 2D TMC interlayer at the perovskite/$PC_{70}BM$ interface, highlighting their potential in improving charge extraction in PSCs.

Lifetime measurements

The stability of the PSCs incorporating TMC nanosheets was investigated following the International Summit on Organic Photovoltaic Stability (ISOS) L-2 protocol. Thus, the devices were subjected to continuous 1 sun illumination under ambient humidity at 65 °C.[100] Fig. 4 illustrates the normalized PCE of the unencapsulated devices over time. The reference device exhibited a burn-in phase during the initial testing period and a fast degradation afterwards. This behavior can be attributed to the degradation of the Ag electrode caused by its reaction with iodine, which migrated from the perovskite layer.[101–103] The device incorporating SnS_2 nanosheets showed the worst stability, while the one containing $MoSe_2$ nanosheets exhibited similar behavior to the reference cell. On the other hand, the incorporation of InSe led to the disappearance of the burn-in phase, enhancing the cell stability. The InSe-incorporating PSC exhibited a T_{70} of 250 h, *i.e.*, the device retained 70% of its initial PCE after 250 h. The superior stability of the InSe-containing PSC compared to the other cells can be correlated with the morphological and chemical properties of InSe nanosheets. The photo-induced degradation of InSe towards In_2Se_3 and In_2O_3 under ambient conditions can commence a surface passivation interlayer at the perovskite/ETL interface. The formation of In_2Se_3 and In_2O_3 (ref. 104) does not seem to affect the PCE and enhances the stability of the device, according to our results. Moreover, the InSe nanosheets show the highest lateral size amongst the investigated flakes (Fig. S1†) and therefore, InSe can serve as an effective barrier, protecting the metal electrode from the degradation species of the perovskite, thus enhancing the device stability.

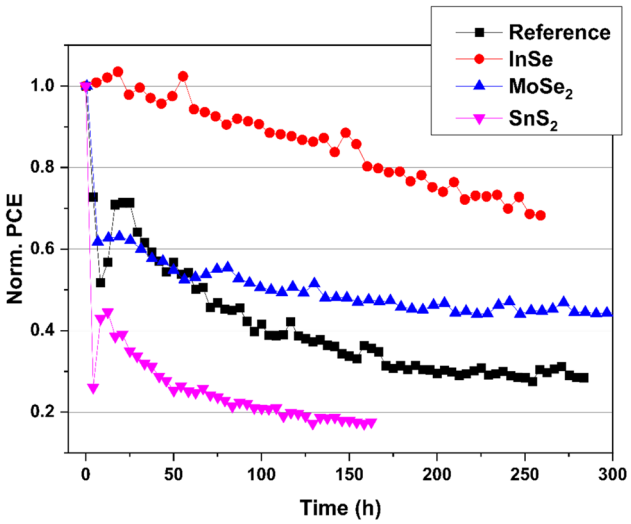

Fig. 4 Stability measurements of the PSCs incorporating InSe, $MoSe_2$, and SnS_2 interlayers under continuous 1 sun illumination, ambient humidity and 65 °C temperature (ISOS L-2).

Conclusions

The structure of inverted PSCs has been systematically optimized by screening the incorporation of various 2D TMCs in the form of an interlayer between the perovskite and the $PC_{70}BM$ ETL. Specifically, bulk InSe, SnS_2, and $MoSe_2$ were exfoliated by means of ultrasonication-assisted LPE and deposited atop the perovskite surface by spin coating to form thin (nanometer-thick) films. The incorporation of TMC interlayers causes a shift in the energy levels towards lower energies, altering the energy level offset at perovskite/charge-transporting layer interfaces. In detail, the introduction of SnS_2 and InSe nanosheets reduces the energy offset at the perovskite/$PC_{70}BM$ interface, resulting in an increase of the FF and PCE of the devices. The SnS_2- and InSe-incorporating devices exhibited relative improvement in PCE by 5.05% and 3.37%, respectively, compared to reference (without 2D TMCs) cells. The PSCs engineered with the SnS_2 interlayer showed the highest PCE, reaching 18.5% and FF of 82%. Conversely, the $MoSe_2$ interlayer introduces a small cliff arrangement at the interface of perovskite/$PC_{70}BM$. Compared to reference cells, the cells of $MoSe_2$-incorporating devices demonstrated improved PCE compared to reference cells, increasing the J_{sc} and V_{oc}. Moreover, to assess the long-term stability of the cells, the devices were subjected to continuous 1 sun illumination at 65 °C, following the ISOS-L2 ageing protocol. The results indicate different stability behaviors of the cells incorporating the investigated TMC interlayers, reflecting the different physico-chemical properties of the 2D TMCs. The incorporation of the $MoSe_2$ interlayer has no discernible effect on device stability, while the SnS_2 interlayer has a negative impact. On the other hand, InSe interlayer eliminates the burn-in degradation observed in the reference devices, significantly improving the overall cell stability. In summary, this work elucidates the potential of 2D TMCs to engineer the architecture of inverted PSCs.

Conflicts of interest

There are no conflicts of interest to declare.

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