Highly stable and efficient inverted planar perovskite solar cells (PSCs) are fabricated based on a molybdenum disulfide (MoS$_2$) hole extraction interlayer. The performance improvement is attributed to improved hole extraction, while the enhancement in the long-term stability is attributed to the stabilization of the HTM/Perovskite interface, inhibiting the bulk degradation process of the MAPbI$_3$ structure itself.

**Keywords:** perovskite solar cell, molybdenum disulfide, hole extraction interlayer, high continuous operating lifetime, transient electrical characterization

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Abstract

Solution processed organic-inorganic lead halide perovskite solar cells (PSCs) are considered as one of the most promising photovoltaic technologies thanks to both high performance and low manufacturing cost. However, a key challenge of this technology is the lack of ambient stability over prolonged solar irradiation under continuous operating conditions. In fact, only a few studies (carried out in inert atmosphere) already approached the industrial standards. Here, we show how the introduction of MoS$_2$ flakes as a hole transport interlayer in inverted planar PSCs results in a power conversion efficiency (PCE) of ~17%,
overcoming the one of the standard reference devices. Furthermore, this approach allows the realization of ultra-stable PSCs, stressed in ambient conditions and working at continuous maximum power point. In particular, the photovoltaic performances of the proposed PSCs represent the current state-of-the-art in terms of lifetime, retaining 80% of their initial performance after 568 hours of continuous stress test, thus approaching the industrial stability standards. Moreover, we further demonstrate the feasibility of our approach by fabricating large area PSCs (0.5 cm² active area) with MoS₂ as the interlayer. These large area PSCs show improved performance (i.e., PCE=13.17%) when compared with the standard devices (PCE=10.64%).

Introduction

Hybrid perovskite/semiconductor materials due to their exceptional optoelectronic properties[1] are in the spotlight of research for the development of low cost and high efficiency next-generation photovoltaics[2]. Perovskite solar cells (PSCs) with power conversion efficiency (PCE) exceeding 22% have already been demonstrated,[3] having the potential to be further increased.[4] Besides the high PCEs, mostly obtained with a mesoscopic structure,[2] the exploitation of inverted planar heterostructure and hysteresis-free[5] PSCs can also be realized on flexible substrates.[6]

Currently, the main issue of PSCs is the low device lifetime under continuous operating conditions in air, i.e. constant light exposure at maximum power output under ambient conditions.[7] Recently, the importance of engineering the different interfaces inside the device for the development of both efficient and stable PSCs was highlighted.[8] Regarding the long-term instability of these devices, one of the main reasons is associated with the hole transport material (HTL)/perovskite interface. In particular, the instability is attributed to the use of organic hole transporting materials (HTMs),[9] e.g., Poly(3,4-ethylenedioxythiophene)-
poly(styrenesulfonate) PEDOT:PSS, 2,2′,7,7′-tetrakis(N,N-di-pmethoxyphenylamine)-9,9′-spirobifluorene (spiro-MeOTAD) or poly(triarylamine) (PTAA), which need a doping process with hygroscopic materials to improve their charge transport properties. However, the doping procedure limits the long-term air stability of PSCs due to the deterioration of the HTL/perovskite interface.\cite{10,11,12,13,14,15} Additionally, further improvement of PCEs towards the theoretical limit and scalability are issues that need to be addressed for the commercialization of the PSCs technology.

Solution processed (SP) two dimensional (2D) materials, e.g., graphene, tungsten diselenide (WSe$_2$) or molybdenum disulphide (MoS$_2$) obtained by liquid phase exfoliation, due to their unique (opto)electronic and mechanical properties, are valuable candidates to enhance the performance and stability optoelectronic devices.\cite{16-24} In fact, the exploitation of 2D materials as interfacial layers have already shown promising results in terms of PCE and stability optimization in PSCs.\cite{16,17,18,19,20,21,22,23} In particular, the addition of reduced graphene oxide (RGO) at the interfaces of both the mesoscopic\cite{16,20} and planar\cite{19,22,23} structure PSCs have shown to improve both the PCE and durability of the devices. Additionally, the introduction of nitrogen-doped RGO inside the perovskite layer of mesoscopic PSCs, resulted in higher efficiency compared to the un-doped device, due to the larger formed grains inside the CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) absorber.\cite{18} Moreover, the use of other graphene derivatives (e.g., lithium neutralized graphene oxide and pristine few-layer graphene flakes)\cite{17,21} resulted in higher PCEs and lifetimes in both small and large PSCs as well as in large area perovskite modules, if compared with standard devices. However, the beneficial role of SP 2D transition metal dichalcogenides (TMDs) in PSCs is largely unexploited.\cite{24} In particular, there are no reports in literature using TMDs in inverted planar PSCs.

In this work, we propose the use of MoS$_2$ flakes as HTM and hole extraction interlayer in inverted PSCs. The MoS$_2$ flakes are produced by liquid phase exfoliation of their bulk counterpart. The replacement of PEDOT:PSS HTM with exfoliated MoS$_2$ flakes, resulted in
comparable, but less reproducible PCEs from batch to batch (i.e., PCE of 12.46 vs 12.30 % at maximum). In contrast, when the MoS\(_2\) flakes are introduced in between the state of the art HTM, i.e., PTAA and the halide perovskite absorber, MAPbI\(_3\), the devices PCE and reproducibility is increased (i.e., PCE of 16.89 Vs 16.25 %). This effect is ascribed to the hole extraction process improvement following the addition of MoS\(_2\) at the HTL/perovskite interface. Most importantly, the MoS\(_2\) based PSCs’ lifetime increased significantly, compared with the reference devices. The improvement is attributed to the stabilization of the HTM/perovskite interface, inhibiting the bulk degradation process of the MAPbI\(_3\) structure itself. In particular, encapsulated PSCs with MoS\(_2\) interlayer retained 80% of their initial PCE \((T_{80})\) after 568 hours of continuous illumination at maximum power output in ambient conditions. The obtained result is, to date, the highest ever-reported lifetime for PSCs tested in these conditions. Moreover, the proposed approach is scalable, i.e. realization of large area PSCs (0.5 cm\(^2\)), with the addition of SP MoS\(_2\) flakes, showing an 23.8% increase in average PCEs, i.e., \(\sim13.17\) with respect to the reference devices i.e., \(\sim10.64\%\).

**Results and Discussion**

**2.1 Synthesis and characterization of MoS\(_2\) flakes**

MoS\(_2\) flakes are prepared by means of liquid phase exfoliation of bulk MoS\(_2\) crystals, in ethanol/water mixture 60/40 (see Methods and supplementary information –S.I.- for experimental details). After the ultra-sonication step, we use the sedimentation-based separation approach \(^{[24]}\) to separate the exfoliated MoS\(_2\) flakes from the thicker or un-exfoliated ones. The optical absorption spectrum is reported in Figure 1a. By using the Lambert-Beer law and the absorption coefficient of 3400 lm g\(^{-1}\) \(^{[25]}\) the estimated concentration of MoS\(_2\) flakes is \(\sim0.18\) g l\(^{-1}\). The absorption spectrum of the dispersion shows the main features typical of exfoliated MoS\(_2\) flakes.\(^{[25]}\) The two peaks at \(\sim670\) nm and at \(\sim600\) nm.
nm are due to A and B excitonic transitions at the K-point of the Brillouin zone, respectively.\cite{26} The absorption onset at \( \sim 500 \) nm, is due to band to band transitions from the valence to the conduction band.\cite{27} Furthermore, the calculated optical band gap of the MoS\(_2\) flakes is presented in the inset to Figure 1a. An optical band gap of \( \sim 1.78 \) eV is obtained using the exfoliated MoS\(_2\) flakes in dispersion.

The electronic properties of the MoS\(_2\) flakes are determined using ultraviolet photoelectron spectroscopy (UPS) as depicted in Figure S1a. The work function (WF) is calculated from the high binding energy cut-off (\( E_{\text{HBEC}} \)) region (Figure S1b), which for MoS\(_2\) thin film is 3.94 eV, using the equation:\cite{28,29}

\[
WF = h\nu - E_{\text{HBEC}}
\]

where, \( h\nu \) is the He(I) excitation energy, equal to 21.22 eV. The valence band maximum (VBM) can be calculated from the low binding energy cut-off region (\( E_{\text{LBEC}} \)) (Figure S1c) using the equation:\cite{28,29}

\[
\text{VBM} = -(E_{\text{LBEC}} + WF)
\]

For the MoS\(_2\)-thin film the VBM is calculated to be -5.41 eV vs vacuum level, which is near to the one of the MAPbI\(_3\) perovskite absorber (-5.43 eV). This confirms that MoS\(_2\) flakes are an ideal candidate to serve as HTM in MAPbI\(_3\) based-PSCs. The conduction band minimum (CBM) of the MoS\(_2\) flakes is calculated to be \( \sim -2.73 \) eV, considering also the large exciton binding energy (\( \sim -0.9 \) eV) of MoS\(_2\).\cite{30} Comparing the CBM of both, MAPbI\(_3\) (-3.93 eV) and MoS\(_2\) (-2.73 eV), it is expected that the inclusion of MoS\(_2\) layer besides facilitating the hole extraction, also acts as a very efficient electron blocking layer.

An important step to assess the use of MoS\(_2\) in PSC, is to compare the transmittance spectra of the state-of-the-art PEDOT:PSS HTM with the MoS\(_2\) deposition (optimum conditions, see Table S1) on glass/ITO (Indium-Tin-Oxide) substrates.\cite{15} As presented in Figure S2, MoS\(_2\) shows \( \sim 5\% \) (at the maximum point) lower transmittance in the 450–700 nm range, compared with PEDOT:PSS, because of its optical narrow bandgap (\( \sim 1.8 \) eV). However, due to the low
value of transmittance drop, together with the fact that there are two regions in the spectrum (700-800 nm and 400-450 nm) where MoS$_2$ has $\sim$5% higher transmittance compared to PEDOT:PSS, it is expected that both materials have similar parasitic absorption against the hybrid perovskite absorber.\textsuperscript{[15]}

The morphology, \textit{i.e.}, lateral size and thickness, of the MoS$_2$ flakes sample is characterized by means of transmission electron microscopy (TEM). Figure 1b shows a representative TEM image of MoS$_2$ flakes, while the flakes main lateral size distribution population is found at $\sim$240 nm (with a lognormal standard deviation of 0.53), see Figure 1c. The thickness of the MoS$_2$ flakes sample is analysed by atomic force microscopy (AFM). Figure 1d shows a representative topographic AFM image, while the statistical thickness distribution is reported in Figure 1e. The flakes thickness maximum population peaks at 1.03 nm (lognormal std. dev. 0.73).

Raman spectroscopy is a non-destructive and powerful tool for determining the doping, presence of defects and the average number of layers of TMDs flakes.\textsuperscript{[31]} In particular, the Raman spectra of the MoS$_2$ consists of first-order modes at the Brillouin zone centre $E_{2g}^{1}(\Gamma)$, located at $\sim$379 cm$^{-1}$ and $A_{1g}(\Gamma)$, $\sim$403 cm$^{-1}$, involving the in-plane displacement of Mo and S atoms and the out-of-plane displacement of S atoms, respectively.\textsuperscript{[33]} The typical Raman spectra of MoS$_2$ flakes present a shift of the $E_{2g}$ and $A_{1g}$ peaks, compared with the bulk counterpart, changing the distance between both peaks from 26 cm$^{-1}$ for bulk MoS$_2$ to 19 cm$^{-1}$ in the monolayer form.\textsuperscript{[32]} The MoS$_2$ Raman spectrum of exfoliated sample is reported in Figure 1f. The spectrum shows a red shift for both vibrational modes, $E_{2g}^{1}$ and $A_{1g}$ with respect to the bulk counterpart. The red shift of the in plane mode $E_{2g}^{1}$ indicates adsorption of solvent molecules on thin MoS$_2$ flakes, a typical behaviour in chemically-assisted exfoliated flakes,\textsuperscript{[33]} while the red-shift of the out of plane $A_{1g}$ mode is due to the decreased flake thicknesses.\textsuperscript{[34]} The TEM, AFM and Raman characterization demonstrates that the dispersion consists of nanometric few-layer MoS$_2$ flakes.
Figure 1. Characterization of the exfoliated MoS$_2$ flakes. (a) Optical absorption spectrum. Inset: calculated optical band gap of the MoS$_2$ flakes. (b) TEM image of a representative MoS$_2$ flake. (c) Statistical analysis of the MoS$_2$ flake lateral size distribution. (d) AFM image of selected MoS$_2$ flakes and (e) statistical distribution of the MoS$_2$ flakes thickness. (f) Raman spectroscopy of bulk (black curve) and exfoliated MoS$_2$ (blue curve) flakes.

2.2 Photovoltaic performance and electro-optical characterization

In order to verify the photovoltaic performances improvement following the MoS$_2$ flakes addition in inverted PSCs, the architecture ITO/HTM/MAPbI$_{3-x}$Cl$_x$/PCBM/PFN/Al (Figure 2a) is fabricated, by exploiting PEDOT:PSS and MoS$_2$ as HTM. The energy levels of the different materials used in the device stack, including that of MoS$_2$, are presented in Figure 2b,\cite{35} showing the close match between the VBM of MoS$_2$ and the hybrid perovskite, which indicates energy barrier-free hole extraction.
Figure 2. Structure, performance and photoluminescence response of the PSCs. Schematic (a) device architecture and (b) energy-band diagram under flat-band conditions of the fabricated planar inverted PSCs. (c) The J-V curves of PSCs based on PTAA (black) and PTAA/MoS$_2$ bilayer (red) HTMs measured under AM 1.5G (100 mW cm$^{-2}$) illumination. (d) PCE distribution of the devices with (red) and without (black) MoS$_2$ interlayer extracted from 20 identical devices. (e) External quantum efficiency spectra and integrated $J_{SC}$ of the PTAA (red) and PTAA/MoS$_2$ (black) based devices. (f) Photoluminescence spectra (excitation at 543 nm) of CH$_3$NH$_3$PbI$_3$/PTAA (black) and MoS$_2$/PTAA/glass (red) substrates.

The current density-voltage (J-V) curves of the PEDOT:PSS and MoS$_2$ HTM based PSCs using the MAPbI$_{3-x}$Cl$_x$ as the photo-absorber is shown in Figure S3a. The optimization for the preparation of the MAPbI$_{3-x}$Cl$_x$ has been examined in previous papers,$^{22,36}$ although a
single spin coating step of the MoS\textsubscript{2} dispersion onto ITO leads to improvement of the PCE compared to the HTM-free device, the PCE measured (\textit{i.e.}, 7.80\%) is by far lower with respect to that achieved by the PEDOT:PSS HTM-based ones (\textit{i.e.}, 12.30\%), see Table S1. This result is explained by the fact that a single spin-coating step does not provide a uniform and compact MoS\textsubscript{2} layer, covering completely the ITO substrate. To understand the role of the MoS\textsubscript{2} layer thickness, we carried out sequential spin-coating steps. The optimum conditions are obtained after 6 consecutive spin coatings of the MoS\textsubscript{2}, which provide the ITO substrate coverage. A significant enhancement in the short-circuit current density (\textit{J}_{sc}), from 20.08 to 22.13 mA cm\textsuperscript{-2}, is observed when the MoS\textsubscript{2} is used as HTM, compared with the PEDOT:PSS. On the contrary, for the same devices, a decrease in both open circuit voltage (\textit{V}_{oc}), from 832 to 798 mV, and in fill factor (FF) from 67.3\% to 60.9\% is registered. As a result, the use of MoS\textsubscript{2} as the HTM allows to design PSCs with a PCE that outperformed devices based on the PEDOT:PSS (\textit{i.e.}, 12.46 vs 12.30 \% at maximum), but with low reproducibility (Figure S3b). The improvement in \textit{J}_{sc} of MoS\textsubscript{2}-based PSCs is thus further investigated and confirmed using external quantum efficiency (EQE) and photoluminescence (PL) spectroscopy (Figure S4 a,b).\textsuperscript{[22]}

In order to improve both the PCE values (~12.5\%) and the reproducibility, we investigated the influence of the MoS\textsubscript{2} as an interfacial layer of inverted PSCs, exploiting the structure ITO/HTM/MoS\textsubscript{2}/Perovskite/PCBM/PFN/Al. Due to the fact that the spin-coating of the MoS\textsubscript{2} dispersion washes out the as-prepared PEDOT:PSS film, the non-aqueous processed PTAA HTM doped with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) small molecule is used.\textsuperscript{[37,38]} The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of PTAA are -5.25 and -2.30 eV, respectively (see Figure 2b).\textsuperscript{[39]} Thus, by using the MoS\textsubscript{2} thin film with VBM -5.41 eV as interfacial layer between the PTAA HTM (-5.25 eV) and the perovskite absorber (-5.43 eV), the hole extraction and the performance of the device could be potentially improved.
The transmittance spectra of PTAA and PTAA/MoS$_2$ (using the optimum conditions, see Table 1) on glass/ITO substrates are compared. The reduction in transmittance is $<$3% (at the maximum point) in the 450–700 nm range (Figure S5), as in the case of MoS$_2$ used as HTM. Thus, the parasitic absorption from the MoS$_2$ thin film can be considered negligible.

Figure 2c displays the current density-voltage ($J$-$V$) curves of the PTAA and PTAA/MoS$_2$ HTM-based PSCs using now the sequentially deposited MAPbI$_3$ as the photo-absorber. In this configuration, the thickness of the MoS$_2$ thin film has less influence on the performance of the device, if compared with the configuration of MoS$_2$ used as HTM. The introduction of MoS$_2$ thin-films as interlayer between the PTAA and MAPbI$_3$ has a dual function. On one hand, it improves the PCE of inverted PSCs from 15.51 to 16.42 % (i.e. 6% enhancement, see Table 1), a significant increase of the $J_{sc}$ (from 20.05 to 20.71 mA cm$^{-2}$) and FF (from 76.63 to 78.41 %) are also observed, while no significant change is observed for the $V_{oc}$ value (1010 vs 1011 mV). On the other hand, an improvement in the device reproducibility (Figure 2d), which is a remarkable issue in the MoS$_2$ based HTM PSCs, is achieved. The standard deviations of the electrical parameters for both PSCs are calculated by fabricating 5 identical PSCs for each type, consisting of 4 solar cells each.

<table>
<thead>
<tr>
<th>HTM</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>Average PCE (Max.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTAA</td>
<td>20.05±0.48</td>
<td>1010±13</td>
<td>76.63±0.77</td>
<td>15.51 (16.25)</td>
</tr>
<tr>
<td>PTAA/MoS$_2$ (1 spin)</td>
<td>20.35±0.49</td>
<td>1010±10</td>
<td>77.88±0.61</td>
<td>16.01 (16.68)</td>
</tr>
<tr>
<td>PTAA/MoS$_2$ (2 spins)</td>
<td>20.71±0.35</td>
<td>1011±7</td>
<td>78.41±0.39</td>
<td>16.42 (16.89)</td>
</tr>
<tr>
<td>PTAA/MoS$_2$ (3 spins)</td>
<td>20.61±0.39</td>
<td>1009±8</td>
<td>78.11±0.35</td>
<td>16.24 (16.75)</td>
</tr>
</tbody>
</table>

External Quantum Efficiency spectrometry is performed to confirm the enhancement of the $J_{sc}$ in the PTAA/MoS$_2$, compared with the neat PTAA-HTM-based device (Figure 2e). The bilayer PTAA/MoS$_2$ HTM exhibits a broad and uniform increase in EQE, in the entire spectral range measured. Considering that the introduction of MoS$_2$ flakes in a thin-film form reduces the energetic offset between PTAA and MAPbI$_3$, due to the VBM alignment of MoS$_2$ and MAPbI$_3$. This $J_{sc}$ enhancement can only be explained in terms of an optimized charge
injection and collection with respect to the reference device.\textsuperscript{[22]} The integrated $J_{sc}$ extracted from the EQE differs by \(~4\%\) compared to the actual measured $J_{sc}$ values (see Table 1), indicating good accuracy of our electrical measurements.

In order to get an insight about the charge extraction properties of the photo-generated carriers from the MAPbI$_3$ to the two different HTM systems, \textit{i.e.}, the PTAA and PTAA/MoS$_2$, the samples steady state PL spectra are measured and analysed (Figure 2f). The PL spectra are collected from perovskite films fabricated on glass/HTM substrates. The MAPbI$_3$ perovskite film deposited on PTAA/MoS$_2$ thin film promotes a PL quenching, compared to the PTAA films, proving that MoS$_2$ interfacial layer enhanced the carrier extraction rate at the HTM/perovskite interface.\textsuperscript{[22]} Moreover, the introduction of MoS$_2$ as interfacial layer improves the reproducibility of the PL measurements (see error bar in Figure 2f). The PL data further supports our findings from the I-V and EQE spectra, suggesting that the use of MoS$_2$ as interlayer between the HTM and the perovskite absorber in PSC enhances both the $J_{sc}$ value and the reproducibility of the device.

To gain further insight into the PCE enhancement resulting from the introduction of MoS$_2$ hole extraction interlayer, the charge-transfer/extraction and charge recombination kinetics in PSCs with and without MoS$_2$ are tested. In Figure 3a is displayed the transient photocurrent (TPC) decay under short-circuit conditions in order to understand the influence of MoS$_2$ interlayer on the charge transfer properties in solar cells.\textsuperscript{[40]} The photocurrent decay lifetimes are calculated to be 2.97 and 2.63 $\mu$s for the devices without and with the use of MoS$_2$ thin film, respectively. The obtained values are calculated by using a single exponential decay fit. The slightly shorter delay time (~12\%) of the MoS$_2$-based device compared with that of MoS$_2$-free device indicates a boost of the hole carrier extraction with the inclusion of MoS$_2$ in the PSCs, a data consistent with the PL measurements.\textsuperscript{[40]} Additionally, the transient photovoltage (TPV) decay under the open-circuit condition of both devices is measured to characterize the PSCs. TPV decay measurements indicate the recombination velocity of
injected electrons, from which the charge carrier lifetime can be extracted. A fast photovoltage decay indicates rapid recombination. As shown in Figure 3b, it is found that the charge-recombination lifetime (τ_r) of the device with MoS_2 is slightly longer than that of the device without MoS_2 (i.e., 35μs for MoS_2-based vs 29 μs for MoS_2-free PSCs, calculated using a single exponential decay fit of the experimental data). The lower charge carrier recombination velocity in the MoS_2 device, compared with the reference one, further supports the improved carrier extraction from perovskite layer to the PTAA HTL due to the band alignment optimization induced by the presence of MoS_2 interfacial layer.

![Figure 3.](image)

**Figure 3.** (a) Normalized transient photocurrent decay and (b) normalized transient photovoltage decay of PSCs with and without MoS_2 hole extraction interlayer.

To further support the results of TPC and TPV decay measurements, the light intensity-dependent J–V characteristics and the TPV rise profile of the PSCs with and without MoS_2 interlayer are investigated. The dependence of J_{SC} on the light intensity is presented in Figure 4a. From the Schottky equation can be derived that:

\[
V_{OC} = \frac{n k T}{q} \ln \left( \frac{J_{SC}}{J_0} \right) = \frac{n k T}{q} \ln(I^\alpha) + C
\]

where J_{SC} is the photocurrent, I is the illumination intensity, C is a constant and \( \alpha \) is an empirical parameter which is derived from the slope of J_{SC} against the illumination intensity. The ideal solar cell without bi-molecular recombination from free carriers should display an \( \alpha \) value very close or equal to unity. Also, a nonlinear trend of J_{SC} versus
light intensity is linked with the existence of energy barriers within the device, negatively affecting the charge extraction process.\cite{17,21} By fitting the experimental data with a power law, $\alpha$ values of 0.993, and 0.968 are obtained for devices with and without MoS$_2$ interlayer, respectively. The introduction of MoS$_2$ at the HTL/perovskite absorber interface reduces the bimolecular recombination, thus the free charges are more efficiently extracted by the PTAA hole transporter.\cite{41,17,21} As a final crosscheck regarding the role of MoS$_2$ interlayer in the charge carrier recombination/extraction dynamics within the PSCs, the TPV rise test is carried out and reported in Figure 4b. The transient rise time of the $V_{OC}$ is generally correlated with the electron transfer from the perovskite to electron transporter, and the hole transfer from the perovskite to the hole transporter.\cite{21} The PSCs with MoS$_2$ hole transport interlayer have shown faster $V_{OC}$ rise time with respect to the reference cell, indicating a more efficient hole transfer at the PTAA/MoS$_2$/perovskite interface if compared with the PTAA/perovskite one.\cite{21}

![Figure 4](image_url)

**Figure 4.** (a) $J_{SC}$ and (b) Normalized $V_{OC}$ rise profile acquired by retaining the devices with and without MoS$_2$ interlayer in open circuit condition, in the dark and by suddenly (t=0) switching on the light at 1 SUN irradiation condition.

### 2.3 Stability measurements of unsealed solar cells

It has been recently demonstrated that inverted PSCs using PTAA as the HTM is an effective structure to obtain high PCE values.\cite{38} However, there are no reports about the lifetime of these efficient inverted PSCs under ambient conditions. The stability measurements of the PSCs with and without the addition of MoS$_2$ thin film as the interfacial
layer is presented in Figure 5, under continuous solar illumination and ambient atmosphere. The devices are scanned from short circuit (SC) to open circuit (OC) every 10 minutes with a scan rate of ~27 mV/s. As shown in Figure 5a, the addition of MoS$_2$ as interfacial layer between PTAA and MAPbI$_3$ increased the device stability. In particular, on one hand, the reference PSC shows a significant decay of its PCE which eventually fails after ~12 hours of stress test. On the other hand, the MoS$_2$ incorporated PSCs improved the stability of the device performance, i.e., after ~12 hours of the stress test the device preserved more than 97% of its initial PCE. By analysing the figures-of-merit (FoM) that determine the PCE, i.e., $J_{sc}$, $V_{oc}$ and FF, over time, (Figure 5 b, c, d, respectively), $J_{sc}$ and FF are the FoM that show a large difference between the reference device (PTAA-based one) and the PTAA/MoS$_2$–based one. This implies that the incorporation of MoS$_2$ at the HTL/perovskite absorber interface inhibits the light activated photocurrent degradation,\[^{42}\] stabilizing the perovskite bulk.\[^{22, 38}\]

![Graphs](image)

**Figure 5.** Unsealed perovskite solar cells stability. Evolution of normalized (a) PCE, (b) $J_{sc}$, (c) $V_{oc}$ and (d) FF of PTAA (black) and PTAA/MoS$_2$ (red) HTMs based PSCs under continuous AM 1.5 G illumination (100 mW cm$^{-2}$) in ambient conditions (~50% RH).
In PSCs, the HTM plays a key role because it acts as both charge dissociation/transporting layer, as well as charge recombination suppressor.$^6$ However, PTAA has a low electrical conductivity, thus a doping process with F4TCNQ small molecule is needed to effectively enhance the holes transport.$^{[43]}$ Nevertheless, as discussed above, this doping process determines a trade-off between the PCE and stability.$^{[10]}$

In order to prove this hypothesis, inverted PSCs, with and without MoS$_2$ thin film as interfacial layer, are prepared and characterized. Differently from the previously presented J-V measurements, for these experiments, the PTAA is un-doped (without F4TCNQ small molecule). In Figure S6 are presented the J-V curves of the devices with and without the MoS$_2$ interfacial layer, with the averaged photovoltaic characteristics for each device reported in Table S2. The results show that without the addition of F4TCNQ in the PTAA and PTAA/MoS$_2$, the devices PCE decreased by ~15% for both cells (i.e., PCE of 13.06% and 13.95%, respectively).

Regarding the lifetime of the un-doped PTAA- and PTAA/MoS$_2$-based PSCs, the degradation test is repeated using the same experimental conditions as in the case of the doped PTAA and PTAA/MoS$_2$ (see Figure 5). The un-doped PTAA based device retained ~ 70% of its initial PCE after 12 hours of the stress test, see Figure S7. On the contrary, in the same time scale, the doped device retained only ~20% of its initial PCE. This indicates that the doping of PTAA with F4TCNQ improves the device performance but also activates a process that speeds up the device failure. Even more, the addition of F4TCNQ in MoS$_2$ covered PTAA PSCs, does not have a significant effect for the device degradation. This implies that the MoS$_2$ thin film acts as a barrier for F4TCNQ doped PTAA layer in contact with the perovskite layer, preventing the PTAA film or the perovskite film (or both) degradation. The investigations reported in the following analysis sections will clarify the mechanism at the origin the MoS$_2$ protective role. The decay of J$_{sc}$ and FF parameters for both cells follows a similar trend, with the degradation rate of PTAA/MoS$_2$ PSCs to be ~10% slower. Most importantly, the V$_{oc}$ for
both PSCs maintains the same value during the entire stress test, indicating the preservation of perovskite in the absence of the F4TCNQ dopant.

2.4 Series resistance and conductivity calculations over time

In order to have an insight of the mechanism responsible for the degradation of the F4TCNQ-doped PTAA-based PSCs, when MoS$_2$ is introduced, the series resistance ($R_s$) over time of the devices are determined, see Figure S8. The PTAA-based device has shown a $\sim$7-fold increase in the $R_s$ value after 12 hours of continuous stress test, while the $R_s$ of the PTAA/MoS$_2$-based PSCs, in the same time scale did not change. The contact resistance between the semiconductor and the electrodes mainly contribute for the solar cells $R_s$.\cite{21,22}

The optimization of the interfaces between the semiconductor material and the electrodes plays a crucial role for the solar cells operation, and in particular for PSCs.\cite{21} Accordingly, the optimization of the ITO/HTM/MAPbI$_3$ interface is vital, since an ohmic contact is required for the transportation of photo-excited holes from the perovskite towards to the ITO.\cite{22} The $R_s$ behaviour could be linked with the fact that the reference devices HTM/Perovskite interface is significantly degraded after the stress test, thus increasing the electrical resistance, while the one of the MoS$_2$-based devices remained unchanged after the stress test.

With the aim to understand the mechanism of the failure on the reference-device with the increase of the $R_s$, we calculated the direct current (DC) conductivity ($\sigma_0$) of the different HTMs over time, using the equation $I = \sigma_0 A d^{-1}V$.\cite{22} This is carried out by measuring the I-V characteristics of sandwiched cells composed by ITO/HTM/Au, with PTAA or PTAA/MoS$_2$ thin films (both doped with F4TCNQ) used as the HTMs. The as-prepared cells are scanned $i.e.$, the I-V curve is obtained every 10 minutes by scanning the cell from -1 to 1 V periodically (Figure S9 a,b). In Table S3 are summarized the results before and after the stress
test of the different PSCs. The $\sigma_0$ of the PTAA HTM, at the end of the stress test, is decreased by $\sim60\%$ with respect to its initial value. After the test, the PTAA/MoS$_2$ bilayer HTM $\sigma_0$ remained almost unchanged ($\sim3\%$ increased). This implies that the introduction of MoS$_2$ interlayer significantly maintained the conductivity of the HTM, which is vital for the device operation, a parameter that correlates the ohmic contact between the semiconductor and the electrode in solar cells.$^{[22]}$ Another point to be noted is the enhancement of $\sigma_0$ after the addition of MoS$_2$ by $\sim40\%$, a result that further supports the enhanced $J_{sc}$ and the quenched PL intensity of such devices.

2.5 Stability investigations using X-ray Analysis

X-ray Diffraction (XRD) is used to both detect structural changes of the perovskite layer and uncover the role of MoS$_2$ as interfacial layer in PSCs. A motivation that triggered the study of the structural properties before and after the stress test is the different trend in $V_{oc}$ decay, shown by both PSCs, PTAA as HTM and MoS$_2$-based devices (PTAA/MoS$_2$ as HTM). The different trend in $V_{oc}$ suggests differences in decomposition, structural changes, in the perovskite layer. For both devices, two set of experiments are performed: the first one on the complete PSC, while the second one on an intermediate step of device fabrication ($i.e.,$ PSC without the metal electrode). By carrying out the experiment on the incomplete cell, it is possible to discriminate between degradation processes associated to solar irradiation and the ones related to the device operation (stress test: light exposure and voltage application). XRD patterns, collected on the active materials (ITO/PTAA/Perovskite/PCBM) and on the reference-device (ITO/PTAA/Perovskite/PCBM/PFN/Al), are shown in Figure 6 a,b comparing the pristine state (black solid line) and aged state (grey dashed line). The XRD patterns collected on the integrated devices are obtained impinging on the surface a portion covered by the 100 nm-thick Al-electrode.
Figure 6. Crystallinity changes in thin films and devices before and after degradation. (Top) XRD comparison of the pristine state (solid line) and aged state (dashed line) of the (a) Reference devices, on the active materials (ITO/PTAA/Perovskite/PCBM system): (b) Reference-device (ITO/PTAA/Perovskite/PCBM/PFN/Al): XRD study of the MoS$_2$-based devices. (c) on the active materials (ITO/PTAA/MoS$_2$/Perovskite/PCBM system): (d) Reference-device (ITO/PTAA/MoS$_2$/Perovskite/PCBM/PFN/Al)

The XRD peaks, labelled in Figure 6, are attributed to tetragonal CH$_3$NH$_3$PbI$_3$ [Space group I4/mcm (Z=4), a=8.800 Å, c=12.685 Å]. The (211) reflection position, inconsistent with the cubic symmetry, is essential for discriminating between the cubic and tetragonal perovskite phase. The unlabelled peaks are attributed to the ITO substrate signal, as accurately discussed in the S.I. (Figure S10a). The presence of hexagonal lead iodide (PbI$_2$) is also detected [namely the (101) reflection at 2θ = 12.70° (JCPDS 07-0235)], indicating that this component has not been converted into perovskite to its full extent. The ratio of the peak intensities of PbI$_2$ (101) and Perovskite (110) was calculated and resulted in 0.43 for both Reference and MoS2 devices. The beneficial role of unreacted PbI$_2$ in the efficiency of PSCs
has been reported previously.\[47] Additionally, the XRD analysis also addresses the Al electrode stability, an issue which may arise in the case of devices subjected to long term stability tests: the comparison of XRD data collected on the pristine and aged of Reference devices and MoS$_2$–based devices, reported in the S.I. (Figure S10b and Figure S10c ), does not show any modification of the electrode signal after the stress test.

In the patterns collected on the aged reference device, two additional reflections are observed, labelled as (1) and (2) (Figure 6) and interpreted as follows: (1) the diffraction at 2$\theta$ = 10.70 °, corresponds to the formation of monohydrate ($\text{CH}_3\text{NH}_3\cdot\text{H}_2\text{O}$)$\text{PbI}_3$ crystalline (101) reflection (monoclinic $P_{21}/m$ crystal structure), (2) The diffraction at 2$\theta$ = 11.30 °, corresponds to the formation of dihydrate ($\text{CH}_3\text{NH}_3)_4\text{PbI}_6\cdot2\text{H}_2\text{O}$.\[48,49] This is a clear evidence that the perovskite film is affected by water molecules,\[50] forming mono and di-hydrated compounds, migrating from the ITO and F4TCNQ doped PTAA hygroscopic layers, into the inner components of the device (devices and films are stressed in ambient air) following, well-established, stoichiometric equation:\[49]

$$4[(\text{CH}_3\text{NH}_3)\text{PbI}_3] + 4\text{H}_2\text{O} \rightleftharpoons 4[\text{CH}_3\text{NH}_3\text{PbI}_3\cdot\text{H}_2\text{O}] \rightleftharpoons (\text{CH}_3\text{NH}_3)_4\text{PbI}_6\cdot2\text{H}_2\text{O} + 3\text{PbI}_2 + 2\text{H}_2\text{O}$$

In particular, monohydrate is an intermediate product, which can be re-converted, while the formation of dihydrate indicates that the reaction has been “driven further” by prolonged exposure to water.\[51] Such process is associated to the formation of PbI$_2$ and to the release of two water molecules. However, no extra formation of PbI$_2$ is detected, in addition to the initial contribution. This fact is expected, since the PbI$_2$ phase initially formed during hydration is amorphous (or nanocrystalline). Furthermore, the PbI$_2$ (101) and Perovskite (110) peak intensities ratio is now 0.5, clearly indicating that a degradation of the perovskite component occurred.

For comparison, XRD patterns collected on the MoS$_2$-device (ITO/PTAA/MoS$_2$/Perovskite/PCBM/PFN/Al) and on its active materials (ITO/PTAA/MoS$_2$/Perovskite/PCBM system) are shown in Figure 6 c,d. Comparing the
pristine (black line) and aged state (red line) of the cell. The XRD peaks are labelled as previously discussed for the reference device. MoS\textsubscript{2} (100) reflection is observed, in agreement with JCPDS Nr. 37-1492.\textsuperscript{[52]} The XRD patterns show that the perovskite in the pristine and aged state are overlapping and no evidence of the formation of mono and di-hydrated compounds is detected. Furthermore, no indication of crystallographic degradation of MoS\textsubscript{2} is gained. This is an important finding, demonstrating how the use of a MoS\textsubscript{2} interfacial layer is able to stabilize the device architecture inhibiting the degradation pathway observed for the reference device. The mechanism at the origin of such a protective role relies on the MoS\textsubscript{2} ability to capture water molecules. The polymeric PTAA buffer layer allows diffusion of molecules inside its matrix (the migration velocity is proportional to the applied electric field). In fact, due to the molar conductivity of the PTAA buffer, under operation, the applied voltage plays the role of a driving force for water molecules towards the Al electrode. It is worth noting that, in the present case, the migration of water molecules is possible only from the ITO film toward the cathode, since on the opposite side the glass substrate represents a mechanical barrier for cations. Additionally, since F4TCNQ small molecule is a very hygroscopic material, it plays an important role in water uptake in PTAA layer, triggering the degradation process of the perovskite layer in the absence of MoS\textsubscript{2} interlayer. Contrary, by introducing the protective MoS\textsubscript{2} layer, this effect is inhibited. In fact, MoS\textsubscript{2} basal planes are able to trap and intercalate water by strong van der Waals interactions.\textsuperscript{[53,54,55]} The XRD study of the reference device detects a perovskite layer degradation (structural modification), consequent to water uptake. Introducing a MoS\textsubscript{2} interlayer between the HTM and the MAPbI\textsubscript{3}, the water uptake is inhibited preserving the device structural properties over long lasting operating conditions. These findings are in agreement with the $V_{oc}$ trend of the devices in the stability test (\textit{i.e.} the $V_{oc}$ value, which is a FoM to understand the optimal formation of the perovskite layer, of the reference device shows the decay after the stress test, while the $V_{oc}$ value of the MoS\textsubscript{2} based device remains almost unchanged after the stress test).
However, besides the $V_{oc}$ decay difference, between PTAA and PTAA/MoS$_2$ based PSCs (indicating different perovskite layer degradation), the most relevant difference in the decay of photovoltaic parameters of both devices after the stress test, is due to the FF deterioration (and to a minor extend to $J_{sc}$). This indicates different changes at the interfaces of the studied devices. To get an additional insight into the degradation mechanism, the interfacial changes are studied, by performing Energy dispersive x-ray reflectometry (EDXR) analysis in pristine and aged devices with and without MoS$_2$.

2.6 Probing the Perovskite buried interface by EDXR

Energy dispersive x-ray reflectometry is a useful tool detecting interfacial modifications in layered devices.$^{[56,57]}$ For this purpose, EDXR measurements of the reference and the MoS$_2$ integrated devices are performed. In order to probe the HTM interface with the perovskite film, a first measurement is performed impinging with the X-ray probe from the transparent ITO electrode side, while a second measurement is performed impinging with the X-ray probe from the cathode side. The EDXR patterns for the reference and the MoS$_2$ devices (pristine and aged states) are reported in Figure 7 a,b.
Figure 7. Perovskite/HTM and Perovskite/ETM interfacial changes before and after degradation (Top) ITO-side EDXR patterns for the (a) reference and (b) the MoS$_2$ devices (black dots for the pristine devices, grey dots for the aged once). (Bottom) Al-side EDXR profiles (dark-red dots) and Parratt fitting functions (grey lines) for (c) reference and (d) MoS$_2$ devices, respectively; comparison between the pristine and aged state for both devices.

In the reference cell, the EDXR profiles (Figure 7a) for the pristine and aged device remarkably differ. In fact, in the pristine state, the ITO critical edge ($q_c = 0.052$ Å$^{-1}$ corresponding to glass/ITO interface, electron density $\rho_e = 5.6(1) \times 10^{-5}$ Å$^{-2}$,$^{[57]}$ is well-defined. The reflectivity curve slope is consistent with an estimated overall roughness of $\sigma_{\text{pristine}} = 1.5(1)$ nm (taking into account both the ITO/PTAA and the PTAA/Perovskite interfaces). Both, the curve edge shape and the curve slope indicate the presence of sharp interfaces.$^{[56]}$

However, in the aged device the curve edge shape and the curve slope are strongly affected by the device operation: the critical edge gets smoother with respect to the one of the pristine state, indicating a stronger absorption at the interface, and the roughness decreases, $\sigma_{\text{aged}} =$
These observations of a “smoother interface” are compatible with high intermixing at the perovskite buried interface.\cite{58}

On the contrary, considering the MoS$_2$-based device, no differences are observed under operating conditions. The reflectivity profiles (Figure 7b) corresponding to the pristine and aged states are perfectly overlapping (interface intermixing is present in both cases, probably due to the two-steps annealing process undergone for the MoS$_2$ deposition).

Therefore, we can state that an important effect at the perovskite buried interface occurred only in the case of reference device because of device operation: under working conditions, the indium (In) ions migrate from the ITO anode \cite{56} into the polymeric layers. This is considered one of the major phenomena determining the device failure.\cite{59,60} In the reference-device, under the same conditions, the ion migration compromises the PTAA/perovskite interface. In contrast, the introduction of a MoS$_2$ layer prevents the migration of In ions, inhibiting the degradation of the perovskite buried interface. This is attributed at the protective role of MoS$_2$, which is able to hosts an extensive variety of species ranging from Lewis base to alkali metals, via intercalation.\cite{61,62,63,64} These results are in agreement with the FF values of PSCs with and without MoS$_2$ (significantly reduced degradation rate in FF, which is a FoM for proper interfaces in PSCs, of MoS$_2$-based devices compared to the reference devices).

2.7 Probing the electrode buried interface by EDXR

The second EDXR experiment is conducted impinging with the X-ray beam the metal cathode side, by using the same experimental conditions aforementioned. By following this procedure, it is possible to test in the same set of measurement, the Al electrode, the PCBM film and the perovskite layer. Several EDXR patterns are collected at different angles, in order to maximize the contributions to the reflected intensity from each layer constituting the
device. The results are reported in Figure 7 c,d. The comparison of the EDXR patterns, considering the Reference device, evidences that no modification of the morphological properties of the Al/PFN layers occurred. Contrarily, when the MoS$_2$-device is analysed, it is clear the fringes amplitude enhancement after the aging. However, the slope of the reflectivity curve and the oscillation damping is unchanged. These observations suggest an enhancement of the scattering length density contrast at the interface, \cite{56} namely the Al/PFN cathode buried interface in contact with the PCBM layer, in the aged device. Indeed, the Parratt fitting procedure accounts for a higher electron density in the Al-PFN layer, (the PCBM film refractive index is unchanged), as a consequence of device operation. This effect is probably associated to the enrichment of negative charges at the cathode buried interface, because the MoS$_2$ device, being very stable, worked continuously for a prolonged period, differently from the Reference one. In addition to the bulk effect detected by XRD, the EDXR study of the reference device detects a further interface degradation mechanism, under working conditions: the modification of the HTM/perovskite interface.

2.8 Long-term lifetime test under maximum power point tracking of encapsulated devices

Besides the preliminary stability tests of unsealed devices, to further explore the potential of MoS$_2$-based devices, PSCs with and without the MoS$_2$ interlayer are fabricated and encapsulated inside a nitrogen-filled glove box. Their long-term lifetime is recorded in ambient conditions under continuous light exposure, constantly tracking the maximum power output. The stability test includes a number of protocols that must be validated before the devices or modules can be considered for real applications.\cite{65} Succeeding this test is not trivial for PSCs, taking into account the hygroscopic nature of perovskite films, phase instabilities and light sensitivity.\cite{66} The test is applied to devices with and without MoS$_2$
interlayer, until $T_{80}$ is reached. Additionally, J-V scans are taken periodically to extract the device parameters (Figure S11). As shown in Figure 8a, the reference device reached $T_{80}$ after ~171 hours of the applied stress test, showing a monotonic decay in PCE with a rate of ~0.115 % per hour (at the linear part), while, in the same timeframe, the MoS$_2$-based PSC retained ~98% of its initial PCE. In fact, the MoS$_2$-based PSCs reached $T_{80}$ after ~568 hours of continuous stress test, with a decay rate of ~0.045 %/hour (at the linear part). All the reports demonstrating lifetimes using the same exposed conditions are summarized in Figure 8b, taking into account devices stressed in both ambient and inert atmospheres (see also Table S4). Figure 8b indicates the lifetime values of high efficiency PSCs fabricated using both planar and mesoscopic structures, together with the corresponding values of the MoS$_2$-based devices reported in this work. Only two reports can be compared with the presented results, in terms of long term stability. The first one presenting $T_{85}$ lifetime after ~500 hours (with a performance of 21.4%), while the second one presenting $T_{95}$ lifetime after ~500 hours (with a performance of ~14%). However, both PSCs have been tested in inert atmosphere and using Cs$^{[67]}$ and Rb-containing mixed cations$^{[68]}$ perovskites, respectively. In general, MAPbI$_3$ perovskite absorber reported significantly lower lifetimes$^{[69,70,71,72]}$ compared with the multi-cation perovskites, mainly using formamidinium, Cs and Rb.$^{[67,68,73,74]}$ The use of an interface engineering for the formation of 2D/3D organic cation based-perovskite crystal structure, significantly improves the PSCs lifetime,$^{[72]}$ but again is by far inferior compared with the multi-cation PSCs lifetime. However, even the triple cation perovskite, according to the device structure that is introduced, have presented lifetimes between 60 and 500 hours, demonstrating the crucial role of interfacial layers in PSCs lifetime.$^{[67,73,74]}$ Furthermore, it is important to note that using exactly the same device structure presented in this work, Fu et al. reported $T_{70}$ lifetime of ~60 hours stressed in inert atmosphere.$^{[70]}$ Finally, to our knowledge, this is the first report that tested the lifetime of PTAA-based PSCs doped with the highly hygroscopic p-dopant F4-TCNQ in ambient conditions for both encapsulated and un-
encapsulated PSCs. This is a remarkable result because MoS$_2$ blocked the hygroscopic F4-TCNQ, which facilitate the migration of moisture at the HTM/Perovskite interface and within the perovskite absorber, eventually degrading them. Taking into account the aforementioned considerations, our work open the pathway for PSCs to exceed the industrial standards for stability in the near future.

**Figure 8.** Long-term stability of encapsulated PSCs and state of the art lifetimes reported to date. (a) Lifetime test under continuous illumination at the MPP tracking of devices with (red scatter) and without MoS$_2$ (black scatter) in ambient conditions. Inset: actual MPP values obtained for both devices. (b) State of the art lifetimes reported in continuous device operation in the above-mentioned conditions of high efficiency PSCs in both ambient (black marked) and inert conditions (blue marked). With red is marked the contribution of this work.

### 2.9 Scaling-up to large area cells

Finally, we investigated the effect of MoS$_2$ interfacial layer in large area PSCs (0.5 cm$^2$). A motivation to scale up the device area is due to the significantly improved reproducibility in I-V characteristics and PL measurements of the MoS$_2$ incorporated samples. In **Figure 9a** are presented the J-V characteristics of PTAA and PTAA/MoS$_2$ based PSCs of both the small (0.04 cm$^2$ solid lines) and large (dashed lines) area PSCs. In Figure 9b a photograph of the as-prepared large-area PSC is shown. The obtained results are summarized in Table S5. Remarkably, the PCE of the large area cell with the MoS$_2$ interlayer is significantly higher compared to the reference large area cell (13.17% vs. 10.64%) having a higher $V_{oc}$ with
respect to the reference PSC (1009 vs. 949 mV). This could be an indication of a uniform formation of MAPbI$_3$ in large area devices when MoS$_2$ is introduced as interfacial layer.

![Figure 9. Performance of large area PSCs. (a) J-V curves of the large-area cells (0.5 cm$^2$ active area) with (red dash-dot curve) and without MoS$_2$ (black dash-dot curve) measured under AM1.5G illumination with an intensity of 100 mW cm$^{-2}$. (b) Photograph of a large-area cell with the MoS$_2$ interfacial layer.](image)

3. Conclusion

In summary, we demonstrated that the introduction of solution processed MoS$_2$ flakes between the PTAA HTM and the MAPbI$_3$ absorber is an effective approach to enhance the efficiency of inverted PSCs, achieving a record PCE of ~17%. Besides, MoS$_2$ significantly improved the stability of encapsulated devices stressed in ambient conditions under continuous light exposure. The MoS$_2$-based PSCs achieved $T_{80}$ lifetime of 568 hours, which represent the state of the art for PSCs. Such device stability is ascribed to the twofold beneficial role of MoS$_2$, inhibiting both interface and structural aging pathways. Moreover, we also demonstrated the beneficial role of MoS$_2$ in the scalability process of the PSCs, by realizing large-area cells of 0.5 cm$^2$, obtaining PCE higher than 13%. These investigations pave the way towards high efficiency, large area and ultra-stable PSCs with lifetimes approaching the industrial standards.
Experimental Section

_Synthesis of MoS\(_2\) 2D crystals:_ 50 mg of bulk MoS\(_2\) crystals (form HQ graphene) is sonicated (sonic bath VWR\(^\circledR\)) for 6 hours, in 50 ml of a mixture ethanol/water 60:40 in volume. Afterwards, the dispersion is centrifuged for 30 min at 770 g in an Optima\(^\text{TM}\) XE-90 ultracentrifuge, Beckman Coulter (SW32Ti rotor), in order to separate the un-exfoliated material, form the exfoliated ones. The upper 70 % is recovered and stored for characterization.

_Optical Absorption Spectroscopy (OAS):_ The OAS of the MoS\(_2\) dispersion is carried out with a Cary Varian 5000i UV-vis-NIR spectrometer. The dispersion is diluted to 1:10 in ethanol/water (60:40). The ethanol/water solvent baseline is subtracted from the spectra.

_Transmission electron microscopy (TEM):_ The exfoliated flakes morphology, i.e. lateral size, is characterized by TEM JOEL JEM 1011, with an acceleration voltage of 100 kV. The sample preparation is performed diluting the MoS\(_2\) dispersion ethanol. 10 µl of the diluted sample are drop cast on copper grids (200 mesh), and dried in vacuum overnight at room temperature.

_Raman spectroscopy:_ The MoS\(_2\) dispersion is drop-cast onto a 0.5x0.5 cm Si/SiO\(_2\) wafer (LDB Technologies Ltd.) and dried under vacuum. Raman measurements are collected with a Renishaw inVia confocal Raman microscope using an excitation line of 514 nm with a 100X objective lens, and an incident power of \(~\)1 mW on the sample. The spectra are analysed using Wire 4.4 software.

_Atomic Force Microscopy (AFM):_ The dispersions are diluted 1:30 in ethanol. 50 µL of the dilutions are drop-cast onto Si/SiO2 wafers, and let them dry at 50 °C overnight. AFM images are acquired with Bruker Innova\(^\circledR\) AFM in tapping mode using silicon probes (frequency = 300 kHz, spring constant = 40 Nm\(^{-1}\)). The thickness statistic is performed measuring \(~\)100 flakes from the AFM images. Statistical analyses are fitted with log-normal distributions.
Device Fabrication: For the perovskite precursor solutions preparation (CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ and CH$_3$NH$_3$PbI$_3$) details can be found in our previous publication.$^{22,36}$ The PSC reported are fabricated on pre-patterned ITO coated glass substrates (Naranjo Substrates) with dimensions of 20 x 15 mm and sheet resistance of ~20 Ω sq$^{-1}$. The impurities are removed from the ITO/glass through a three-step cleaning process (detergent deionized water, acetone, isopropanol). Before the deposition of the HTL, the substrates are placed inside an ultraviolet ozone cleaner in order to remove the organic contamination and increase the surface hydrophilicity of ITO coated substrates. In the case of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ based PSCs, as the HTLs are used either the aqueous processed PEDOT:PSS (Heraeus) or the prepared MoS$_2$ dispersion. PEDOT:PSS is spin cast at 4000 rpm for 60 s and then annealed at 120 °C for 15 minutes, while MoS$_2$ thin film is prepared by spin casting the dispersion at 2000 rpm for 45 s for several times to achieve the desired thickness. Between each spin coating step the as prepared film is annealed at 100 °C for ~1 min. Contrary, in the case of the CH$_3$NH$_3$PbI$_3$ based PSCs, as the HTL is used the polymer PTAA (10 g L$^{-1}$ in toluene) doped with 1.5% F4TCNQ small molecule. The PTAA thin film is prepared by spin casting the solution at 4000 rpm for 35 s, following by an annealing of the as prepared thin film at 110 °C for 10 minutes. Following the deposition of PTAA, the MoS$_2$ dispersion is spin cast at 2000 rpm for 45 s for two consecutive times. Afterwards, the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ precursor solution is deposited onto PEDOT:PSS or MoS$_2$ thin films and the CH$_3$NH$_3$PbI$_3$ is deposited onto PTAA or PTAA/MoS$_2$ thin films according to our previously developed methods.$^{22}$ Then, a 2% phenyl-C61-butyric acid methyl ester (PCBM) in chlorobenzene solution is coated onto the perovskite layers at 1000 rpm. After that, 0.04% polyelectrolyte poly[(9,9-bis(30-(N,N-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) in methanol (with a small amount of acetic acid) is spin-coated on PCBM layer at 2000 rpm. Finally, the devices are transferred to vacuum chamber for Al electrode evaporation.
Device characterization and measurements: The performances of the devices are measured under inert atmosphere with an Air Mass 1.5 Global (A.M. 1.5 G) solar simulator at an intensity of 100 mW cm\(^2\) using an Agilent B1500A Semiconductor Device Analyser. A reference monocrystalline silicon solar cell from Newport Corp. is used to calibrate the light intensity. For the degradation study of the un-encapsulated devices, the as-fabricated cells are exposed in continuous solar irradiation, using an A.M. 1.5 G solar simulator, under ambient conditions with relative humidity (RH) constantly above 50% and data plots are obtained by periodically scanning the devices from SC to OC. For the long-term stability tests of the sealed cells, the devices are prepared and encapsulated, using an UV-curable epoxy and a glass coverslip, inside a nitrogen filled glove box. Afterwards, the cells maximum power point is tracked by a modular testing platform (Arkeo - Cicci research s.r.l.) composed by a white LED array (4200Kelvin) under ambient conditions. The LED intensity is calibrated at the equivalent of 1 Sun intensity by adjusting the \(J_{sc}\) value to be equal with the measured in the J-V curve using the solar simulator. The external quantum efficiency measurements are conducted immediately after device fabrication using an integrated system (Enlitech, Taiwan) and a lock-in amplifier with a current preamplifier under short-circuit conditions. The light spectrum is calibrated using a monocrystalline photodetector of known spectral response. The PSCs are measured using a Xe lamp passing through a monochromator and an optical chopper at low frequencies (~200 Hz) in order to maximize the signal/noise (S/N) ratio. Micro-photoluminescence (μPL) studies at 295 K are performed using a setup in backscattering geometry, with a He-Ne 543 nm continuous wave laser as an excitation source. With a microscope objective lens (Mitutoyo 50X) the laser beam is focused down to 1 μm on the sample, placed on an XYZ translation stage, at normal incidence. A spatial filter system is used to obtain the central part of the beam and acquire a uniform energy distribution. In a typical μPL experiment, different excitation positions of the samples are checked with low laser power (controlled by a neutral density filter). The illumination intensity dependence of
J_{sc}, TPV decay and rise and TPC decay measurements are performed with a modular testing platform (Arkeo - Cicci research s.r.l.) composed by a white LED array (4200Kelvin) tuneable up to 140 mWcm$^2$ of optical power density and a high speed source meter unit (600 Ksamples/s) in a four wire configuration.\cite{21} The transmittance spectra are recorded using a Shimadzu UV-2401 PC spectrophotometer over the wavelength range of 300-800 nm. The Ultra Violet Photoelectron Spectroscopy (UPS) studies are performed in a UHV chamber with a SPECS LHS-10 hemispherical electron analyser. The UPS spectra are obtained using HeI irradiation with $h\nu = 21.22$eV produced by a UV source (model UVS 10/35). During UPS measurements the analyser is working at the Constant Retarding Ratio (CRR) mode, with CRR=10. A bias of $-12.29$ V is applied to the sample in order to avoid interference of the spectrometer threshold in the UPS spectra. The high and low binding energy cut-off positions are assigned by fitting straight lines on the high and low energy cut-offs of the spectra and determining their intersections with the binding energy axis. Regarding measurement errors, it should be noted that an error of $\pm0.1$ eV is assigned to the absolute values for ionization energies, work function and other UP-spectra cutoff features where the error margin is significant, due to the process of fitting straight lines.

X-ray diffraction measurements: XRD measurements are performed by means of a Panalytical Empyrean Diffractometer, equipped with a ceramic Cu-anode (40kV-40mA). A parallel plate collimator is used as incident optical pathway to maximize diffracted signal response from layered samples and devices, whilst a unique 2D solid-state hybrid pixel detector (Pix’cel 3D) accomplished the signal detection. The samples, allocated into an Eulerian cradle, are studied in reflection mode and gonio-collections, performed at different angular ranges ($5^\circ < \theta < 80^\circ$).

Energy dispersive X-ray reflectivity measurements: Energy dispersive X-ray reflectivity are performed on an especially designed X-ray spectrometer (Patent No. RM 93 A000410, 1993, R. Felici, F. Cilloco, R. Caminiti, C. Sadun, and V. Rossi Albertini, Italy) characterized by a
non-symmetric configuration, the detection optical path being much longer than the incident one in order to maximize the Reflectivity and reduce the undesired scattering/noise. A polychromatic incident radiation produced by a W-anode is used as probe (operating Energy range 10-55keV), and the reflected signal is collected by means of an energy sensitive Solid State High purity Ge-single crystal detector cooled to cryogenic temperatures by means of an electro-mechanical cooler. The samples are mounted into an appropriate sample holder (transparent to the incident radiation) on top of a two axes cradle used to optimize the reflectivity conditions. A controlled N\textsubscript{2} atmosphere is kept inside the sample holder during the data collection to prevent materials degradation. Experiments are conducted in the following experimental conditions: \( E = 55 \text{ keV}, \ I = 30 \text{ mA} \) and the samples are kept in controlled N\textsubscript{2} atmosphere in an appositely designed sample holder during the completely experimental procedure.

**Supporting Information**

Supporting Information is available from the author.

**Acknowledgements**

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Supporting Information

Extending the continuous operating lifetime of perovskite solar cells with a molybdenum disulfide hole extraction interlayer

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**Figure S1.** (a) HeI Ultra-violet Photo-electron spectra of the drop-casted MoS$_2$ flakes on glass/ITO substrate. The High (b) and Low (c) binding energy cutoffs are also presented for clarity.
**Figure S2.** Comparison of transmittance between PEDOT:PSS (black) and MoS$_2$ (red) thin films on the glass/ITO substrate.

**Figure S3.** (a) The J-V curves of PSCs based on PEDOT:PSS (black) and MoS$_2$ (red) HTMs measured under AM 1.5G (100 mW cm$^{-2}$) illumination. (b) PCE distribution of the devices PEDOT:PSS (black) and MoS$_2$ (red) as HTMs, extracted from 20 identical devices.

**Table S1.** Photovoltaic Parameter of the devices with PEDOT:PSS and MoS$_2$ with different thicknesses HTLs

<table>
<thead>
<tr>
<th>HTL</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>PCE Mean (Max.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>10.11±3.24</td>
<td>701±38</td>
<td>45.6±5.6</td>
<td>3.23 (5.05)</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>20.08±1.32</td>
<td>832±8</td>
<td>67.3±1.1</td>
<td>11.24 (12.30)</td>
</tr>
<tr>
<td>MoS$_2$ (1 spin)</td>
<td>14.21±2.95</td>
<td>767±35</td>
<td>52.6±4.1</td>
<td>5.73 (7.80)</td>
</tr>
<tr>
<td>MoS$_2$ (5 spins)</td>
<td>21.33±1.46</td>
<td>796±33</td>
<td>59.0±3.2</td>
<td>10.02 (11.75)</td>
</tr>
<tr>
<td>MoS$_2$ (6 spins)</td>
<td>22.13±1.43</td>
<td>798±31</td>
<td>60.9±2.9</td>
<td>10.75 (12.46)</td>
</tr>
<tr>
<td>MoS$_2$ (7 spins)</td>
<td>21.84±1.49</td>
<td>797±31</td>
<td>60.0±2.6</td>
<td>10.44 (12.09)</td>
</tr>
</tbody>
</table>
Figure S4. (a) External quantum efficiency spectra of the PEDOT:PSS (black) and MoS$_2$ (red) HTL based devices. (b) Photoluminescence spectra (excitation at 543 nm) of CH$_3$NH$_3$PbI$_3$/PEDOT:PSS (black) and MoS$_2$/glass (red) substrates. In the inset is demonstrated a higher magnification of the Photoluminescence spectra of the MoS$_2$ based sample.

Figure S5. Comparison of transmittance between PTAA (black) and PTAA/MoS$_2$ (red) thin films on the glass/ITO substrate.
Figure S6. The J-V curves of PSCs based on undoped (F4TCNQ-free) PTAA (black) and PTAA/MoS2 bilayer (red) HTMs measured under AM 1.5G (100 mW cm\(^{-2}\)) illumination.

Table S2. Photovoltaic parameters of undoped PTAA and undoped PTAA/MoS\(_2\) based perovskite solar cells

<table>
<thead>
<tr>
<th>Devices</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>(V_{oc}) (mV)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped PTAA</td>
<td>19.09</td>
<td>990</td>
<td>69.10</td>
<td>13.06</td>
</tr>
<tr>
<td>Undoped PTAA/MoS(_2)</td>
<td>20.05</td>
<td>995</td>
<td>69.94</td>
<td>13.95</td>
</tr>
</tbody>
</table>
Figure S7. Evolution of normalized (a) PCE, (b) Jsc, (c) Voc and (d) FF of undoped (F4TCNQ-free) PTAA (black) and PTAA/MoS\(_2\) (red) HTMs based PSCs under continuous AM 1.5 G illumination (100 mW cm\(^{-2}\)) in ambient conditions (~50% RH).

Figure S8. Series resistance trend over time of devices with (red) and without MoS\(_2\) interfacial layer.
Figure S9. I-V characteristics trend over time of (a) ITO/PTAA/Au and (b) ITO/PTAA/MoS$_2$/Au devices both doped with F4TCNQ small molecule.

Table S3. Calculated conductivity values for PTAA and PTAA/MoS$_2$ bilayer before and after the stress test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ (µS/cm)</th>
<th>$\Delta\sigma$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PTAA/Au Fresh</td>
<td>0.0023</td>
<td>-</td>
</tr>
<tr>
<td>ITO/PTAA/Au Aged</td>
<td>0.0009</td>
<td>-60.9</td>
</tr>
<tr>
<td>ITO/PTAA/MoS$_2$/Au Fresh</td>
<td>0.0032</td>
<td>-</td>
</tr>
<tr>
<td>ITO/PTAA/MoS$_2$/Au Aged</td>
<td>0.0033</td>
<td>+3.1.</td>
</tr>
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</table>
Figure S10. a) XRD pattern collected upon the glass/ITO substrate in order to label the diffraction peaks arising from the substrate. Reflections are labelled accordingly to JCPDS File No. 6-416 80. The visible amorphous contribution is attributed to the glass.  

b) XRD patterns of the pristine (black) and aged (blue) Reference Device. ITO and perovskite reflections are labelled in figure as previously discussed. Al electrode signal is also detected [JCPDS: 04-0787]. In the inset the highlight of the Al (1 1 1) [2θ = 38.492°] peak is shown, together with its Gaussian fit. No structural modification of the electrode is detected after prolonged aging, whilst perovskite degradation is clearly visible.  

c) XRD patterns of the pristine (black) and aged (blue) MoS₂ Device. ITO and perovskite reflections are labelled in figure as previously discussed and Al electrode signal is also detected [JCPDS: 04-0787]. In the inset an highlight of the Al (1 1 1) [2θ = 38.525°] peak is shown together with its Gaussian fit. No structural modification of the electrode is detected after prolonged aging.
Figure S11. Normalized (a) $J_{sc}$, (b) $V_{oc}$, and (c) FF trends of PTAA (black) and PTAA/MoS$_2$ based PSCs aged under continuous illumination and maximum power point tracking in a ambient atmosphere.
Table S4. Summary of the reported lifetimes with MPPT in PSCs to date.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Perovskite Absorber</th>
<th>Lifetime @ MPPT (Hours)</th>
<th>PCE (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>MAPbI₃</td>
<td>Tₘ₀ = 148</td>
<td>13.40</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>MAPbI₃</td>
<td>Tₘ₀ = 16</td>
<td>15.42</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>MAPbI₃</td>
<td>Tₘ₀ = 568 (68)</td>
<td>16.9</td>
<td>Current Work</td>
</tr>
<tr>
<td>Inert</td>
<td>MAFAPb(I₀.₈₃Br₀.₁₇)₃</td>
<td>Tₘ₀ = 10</td>
<td>16.5</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>CsMAFAPb(I₀.₈₃Br₀.₁₇)₃</td>
<td>Tₘ₅ = 250</td>
<td>21.1</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>MAPbI₃</td>
<td>Tₘ₀ = 50</td>
<td>15.95</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>(HOOC(CH₂)₄NH₃)₂PbI₄(CH₃NH₃)PbI₃</td>
<td>Tₘ₀ = 150</td>
<td>14.6</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>CsMAFAPb(I₀.₈₃Br₀.₁₇)₃</td>
<td>Tₘ₀ = 60</td>
<td>20.4</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>MAPbI₃</td>
<td>Tₘ₀ = 60</td>
<td>16.1</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>CsMAFAPb(I₀.₈₃Br₀.₁₇)₃</td>
<td>Tₘ₅ = 500</td>
<td>21.4</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>RbCsMAFAPb(I₀.₈₃Br₀.₁₇)₃</td>
<td>Tₙ₅ = 500</td>
<td>14</td>
<td>68</td>
</tr>
</tbody>
</table>

Table S5. Photovoltaic parameters of small (0.04 cm²) and large area (0.5 cm²) cells

<table>
<thead>
<tr>
<th>Devices</th>
<th>Jₛₑ (mA/cm²)</th>
<th>Vₒₑ (mV)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>PCE Drop (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small Area PTAA</td>
<td>20.05</td>
<td>1010</td>
<td>76.63</td>
<td>15.51</td>
<td>-</td>
</tr>
<tr>
<td>Large Area PTAA</td>
<td>18.97</td>
<td>949</td>
<td>59.11</td>
<td>10.64</td>
<td>31.40</td>
</tr>
<tr>
<td>Small Area PTAA/MoS₂</td>
<td>20.71</td>
<td>1011</td>
<td>78.41</td>
<td>16.42</td>
<td>-</td>
</tr>
<tr>
<td>Large Area PTAA/MoS₂</td>
<td>19.35</td>
<td>1009</td>
<td>67.45</td>
<td>13.17</td>
<td>19.79</td>
</tr>
</tbody>
</table>