

Two-Dimensional Material Interface Engineering for Efficient Perovskite Large-Area Modules

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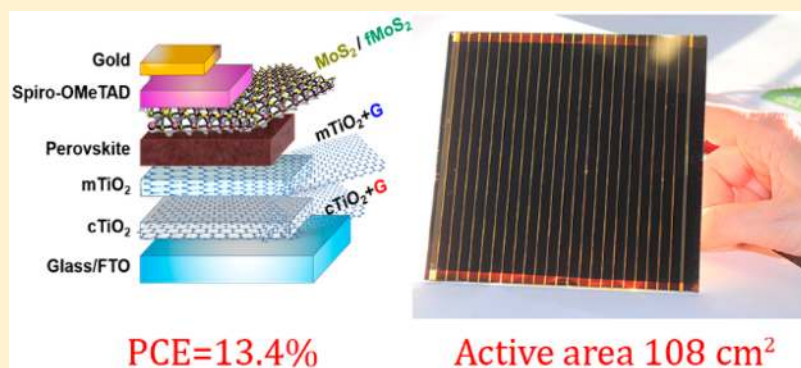
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S Supporting Information



ABSTRACT: In this work, we demonstrate the successful application of two-dimensional (2D) materials, i.e., graphene and functionalized MoS₂, in perovskite solar cells (PSCs) by interface engineering the standard mesoscopic n–i–p structure. The use of 2D materials has the dual role to improve both the stability and the overall power conversion efficiency (PCE) of the PSCs compared to standard devices. The application of 2D materials is successfully extended to large-area perovskite solar modules (PSMs), achieving PCEs of 13.4% and 15.3% on active areas of 108 cm² and 82 cm², respectively. This performance results in record-high active area-indexed aperture PCE (AIAPCE) of 1266.5% cm². In addition, the 2D materials-based PSMs show a stability under a prolonged (>1000 h) thermal stress test at 65 °C (ISOS-D2), representing a crucial advancement in the exploitation of perovskite photovoltaic technology.

In recent years, lead-halide perovskite solar cells (PSCs) have catalyzed the attention of the scientific community, with power conversion efficiency (PCE) exceeding 20%, by using cost-effective and potentially scalable solution processing approaches.^{1,2} In particular, the global research effort boosted the PCE of PSCs up to 24.2% for single-junction³ and 27.3% for tandem perovskite/silicon⁴ solar cells. Despite these important achievements, long-term stability⁵ and scalability⁶ are still the major constraints for the market entry of the perovskite photovoltaic technology.^{7,8} In fact, the photoactive lead-halide perovskites typically lack stability due

to their hygroscopicity and propensity to back-convert into their precursors during exposure to moisture,⁹ oxygen,^{10,11} and light illumination.^{10,12} Moreover, they experience a tetragonal-to-cubic phase transition at the temperature reached during typical solar cell operation (>80 °C),¹³ resulting in making them unfit for standard solar module certifications.^{14,15} In addition, the deposition of both pin-hole-free homogeneous

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41 high-crystallinity perovskite films and effective charge transport
42 layers (CTLs) by industrial approaches is still a tough obstacle
43 toward the development of large-area PSCs with PCE
44 comparable to those achieved by lab-scale (less than few
45 cm^2) cells.^{16–18} In particular, the nucleation and crystal growth
46 kinetics for high-quality perovskite film are attained by
47 optimizing the choice of the solvent^{19,20} and the solvent
48 drying rate²¹ and possibly using antisolvent crystallization.^{22,23}
49 However, this optimization pathway could not straightfor-
50 wardly meet the requirements of large-area linear and/or roll-
51 to-roll (R2R) coatings²⁴ (e.g., doctor blading²⁵ and gravure
52 printing,²⁶ as well as slot-die and spray coating^{27–29}). Beyond
53 the issues relating to the perovskite layer, the choice of the
54 architecture and the interface engineering of the PSCs also play
55 a crucial role in achieving valuable upscaling criteria, since
56 pinhole-free, homogeneous, and, eventually, compact CTLs are
57 mandatory to reduce PCE losses,^{30–34} i.e., to improve the
58 extraction of the photogenerated charge carriers (i.e., the short
59 circuit current density, J_{sc} , and the open-circuit voltage, V_{OC}).³⁵
60 Thereby, both n–i–p planar^{7,36} and mesoscopic architec-
61 tures^{37,38} have been investigated for the realization of large-
62 area PSCs and perovskite solar modules (PSMs),¹⁶ as also
63 reported by several PV companies (e.g., Microquanta Semi-
64 conductor, Solliance, Saule Technologies, and Greatcell Solar,
65 just to cite a few). In favor of the planar structures, these can
66 be produced through low-temperature material deposition
67 processes ($<180\text{ }^\circ\text{C}$), which make feasible the realization of
68 flexible devices produced by using high-throughput R2R
69 techniques.³⁹ So far, the largest solution-processed and
70 efficient PSMs (e.g., aperture area = 16.07 cm^2 and PCE =
71 14.9%)⁴⁰ are based on planar n–i–p architecture, as obtained
72 by depositing a tin oxide (SnO_2)-based electron transport layer
73 (ETL) via spin⁴¹/slot-die coating,⁴⁰ and 2,2',7,7'-tetrakis(*N,N*-
74 di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OME-
75 TAD)-based hole transport layer (HTL) via doctor blad-
76 ing⁴¹/spin coating.⁴⁰ Moreover, a planar architecture based on
77 a SnO_2 ETL and carbazole derivative HTL, demonstrating
78 remarkable stability under 70 mW/cm^2 in the case of small
79 area devices,⁴² achieved a PCE of 14.9% stable over 100 h in a
80 7.25 cm^2 active area mini-module.⁴³ By replacing SnO_2 with a
81 compact TiO_2 ($c\text{TiO}_2$) ETL, as realized by means of high
82 temperature ($450\text{ }^\circ\text{C}$) spray pyrolysis deposition⁴⁴ or e-beam
83 evaporation,⁴⁵ PCE losses have been further reduced to reach a
84 remarkable PCE $>17\%$ on 10.36 cm^2 active area⁴⁴ and a PCE
85 $>10\%$ on an active area of $\sim 170\text{ cm}^2$.⁴⁵ Recently, PSMs based
86 on inverted planar p–i–n architectures have also been
87 produced via electrochemically assembling metal-filamentary
88 nanoelectrodes.⁴⁶ Although these innovative PSMs exhibited a
89 PCE exceeding 14% and a remarkable stability (PCE loss of
90 $\sim 20\%$ after $>180\text{ h}$ at $85\text{ }^\circ\text{C}$ and 85% humidity rate, HR), their
91 active area was limited to 9.06 cm^2 ,^{40,41,44,45} indicating the
92 need to confirm their prompt and facile upscaling. Overall, the
93 aforementioned examples have demonstrated that the planar
94 architectures still face several issues that need to be overcome
95 to design and realize large-area solution processed PSMs with
96 high PCEs. Therefore, it is not by chance that the best
97 performing (both in terms of PCE and stability) large area
98 PSMs (size $>40\text{ cm}^2$) have been demonstrated by using
99 mesoporous architectures.^{17,47} In particular, carbon-based
100 PSMs^{48,49} promise low-cost and superior stability in air
101 compared to their counterparts based on metal contacts.^{48,49}
102 For example, carbon-based PSMs, produced by infiltrating
103 perovskite over $c\text{TiO}_2$ /mesoporous TiO_2 ($m\text{TiO}_2$)/zirconium

oxide (ZrO_2)/carbon paste stacks, having an active area of 47.6
104 cm^2 , have exhibited a stable PCE of 10.1% over more than
105 $10\,000\text{ h}$ under 1 sun illumination.³³ However, when the
106 carbon structure was further scaled up to a record-high active
107 area of 198 cm^2 , the PCE dropped significantly (i.e., 6.6%)⁵⁰
108 due to the irregular infiltration process of the perovskite film.
109 Meanwhile, traditional mesoscopic architectures with metal
110 contacts have been reported for PSMs with record-high
111 PCEs,¹⁷ achieved by engineering the interfaces between the
112 different composing layers. In particular, the interface
113 engineering based on two-dimensional (2D) materials has
114 recently been proposed as an effective way to improve the PCE
115 and the stability of solution-processed PSCs.^{51,52} For example,
116 we have recently proposed graphene interface engineering
117 (GIE) as a strategy to demonstrate PSMs with a PCE of 12.6%
118 on an active area of 50 cm^2 .⁵³ Here, GIE consists of using
119 graphene and graphene-related materials (GRM) in the form
120 of interlayers (also named active buffer layers, ABLs) at
121 perovskite/CTL interfaces and/or as dopant for standard
122 CTLs.^{30,54–58} Previous investigations on mesoscopic n–i–p
123 architectures (glass/fluorine tin oxide (FTO)/ $c\text{TiO}_2$ /graphene-
124 doped $m\text{TiO}_2$ ($m\text{TiO}_2+\text{G}$)/perovskite/spiro-OMe-
125 TAD/gold (Au)) have demonstrated that graphene flakes
126 incorporated into the $m\text{TiO}_2$ have a bifunctional role. On the
127 one hand, they improve the perovskite morphology by
128 reducing the density of the trap states located at the $m\text{TiO}_2$ /
129 perovskite interface,^{54,55} thus limiting the irreversible dissoci-
130 ation of perovskite materials.⁵⁹ On the other hand, they
131 promote the electron extraction from the perovskite to the
132 ETL, as well as the electron transport within the ETLs toward
133 the current collector (i.e., the FTO).⁵⁵ Despite the use of
134 graphene being able to retard the degradation of the
135 perovskite/ETL interface, the instability of the methylammo-
136 nium lead iodide perovskite (MAPbI_3) still represented a limit
137 to pass the standard stress test condition defined by the C450
138 testing protocol for photovoltaic modules.^{60,61} In fact, MAPbI_3
139 undergoes a fast degradation upon exposure to moisture, due
140 to its low formation energy, which causes its decomposition to
141 solid PbI_2 and gaseous methylamine and hydrogen halide
142 under moderate temperature ($60\text{ }^\circ\text{C}$) stresses.⁶² Furthermore,
143 perovskite heating under operating conditions has been
144 reported, causing degradation pathways attributed to atom
145 migration from the Au electrode toward MAPbI_3 .^{22,27} In fact,
146 Au, as well as other electrode metals, can react with MAPbI_3 ,
147 creating nonradiative recombination centers, i.e., PCE losses.⁶³
148 Finally, voltage bias and/or thermal drift also cause the
149 movements of ions composing MAPbI_3 , inducing defects (e.g.,
150 iodine vacancies)^{64,65} that degrade the interface of the device
151 until its failure.⁵⁹

152
153 With the aim to thermally stabilize the most efficient PSCs
154 (as well as the corresponding PSMs), several perovskite
155 absorber optimizations and new device architecture engineer-
156 ing strategies have been proposed.⁶⁶ First, thermally stable
157 mixed-cation hybrid lead halide perovskites using methyl-
158 ammonium (MA), formamidinium (FA), and cesium (Cs)
159 cations have been successfully designed by tuning the
160 Goldschmidt tolerance factor.⁶⁷ Second, novel hole transport
161 materials have been screened for stabilizing perovskite/HTL
162 interfaces.^{61,68} In fact, the well-known weak adhesion of the
163 most established mild organic hole transport materials (e.g.,
164 spiro-OMeTAD or poly(triarylamine), PTAA) to the perov-
165 skite surface^{69,70} can trigger PCE losses.⁷¹ In addition, the poor
166 hole mobility of the spiro-OMeTAD (in the order of 10^{-4} cm^2

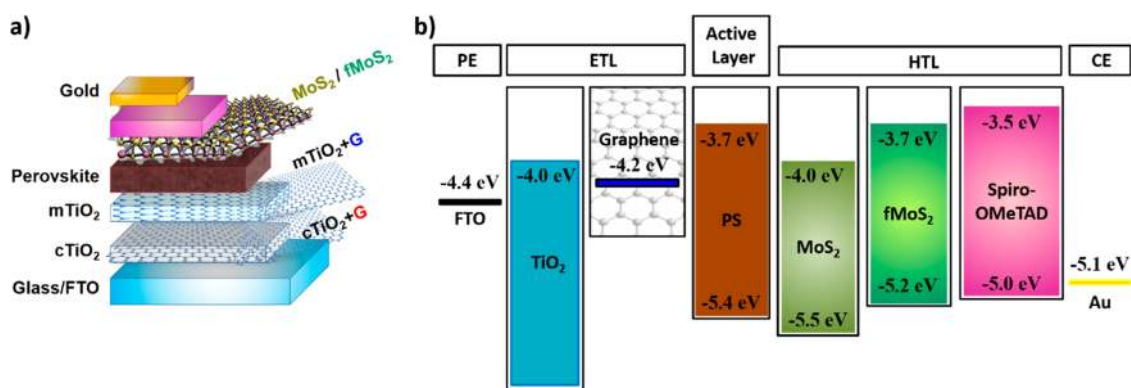


Figure 1. (a) 2D material-engineered PSC architecture and (b) its energy band diagram. The work function values for FTO, TiO₂, and graphene have been taken from refs 77–79. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels for perovskite and spiro-OMeTAD have been taken from refs 80–82, respectively. The energy band edge positions for MoS₂ and fMoS₂ have been experimentally determined by optical absorption spectroscopy and ultraviolet photoelectron spectroscopy measurements, as detailed in the Supporting Information.

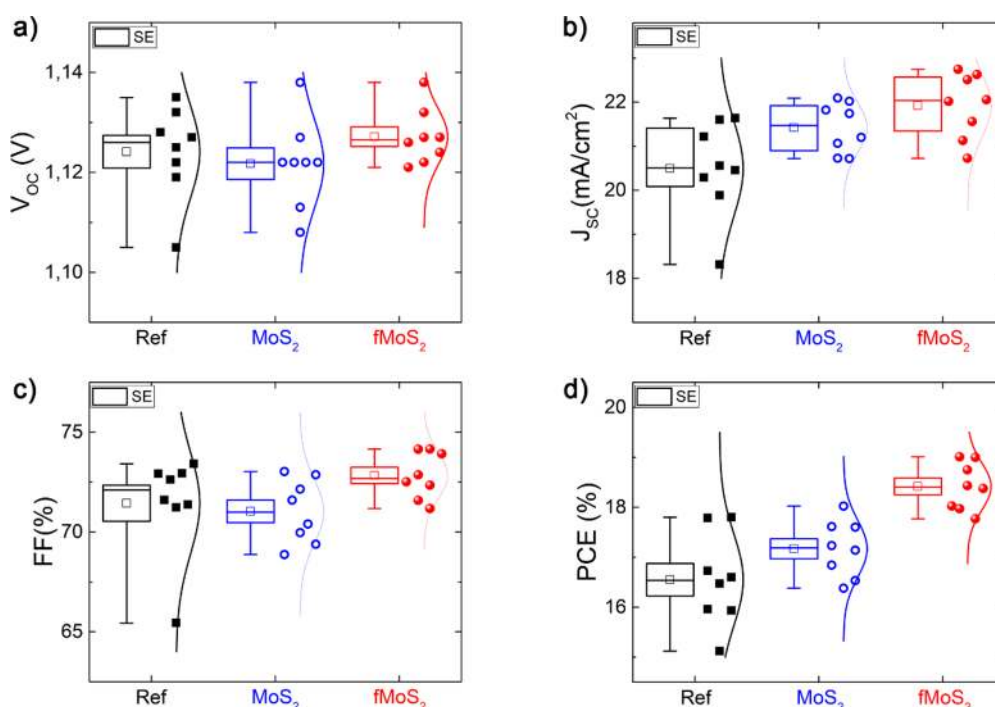


Figure 2. Photovoltaic parameter statistics for the investigated PSCs extracted by the I – V characteristics under 1 sun illumination: (a) V_{OC} , (b) J_{SC} , (c) FF, and (d) PCE. The statistics were measured on 8 PSCs for each architecture.

$V^{-1} s^{-1}$)^{72,73} requires the use of redox active p-type dopants, such as Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI),⁷³ which intensify the device degradation because of their propensity to absorb moisture from the air and become dissolved in the moisture itself.⁷⁴ The photo-oxidation⁷⁵ and the crystallization at temperature > 80 °C⁷⁶ of spiro-OMeTAD can further damage its properties. To eliminate such issues, inorganic hole transport materials, such as copper thiocyanate (CuSCN),^{61,68} have shown improved thermal⁶⁸ and light soaking stability relative to those of organic materials.⁶¹ However, the hazardous solvents (e.g., diethyl sulfide) usually used to disperse CuSCN⁶¹ require a well-controlled environment for the subsequent material deposition, increasing the associated costs in large-scale production chains.

In this work, we report the combination of thermally stable mixed-cation perovskite with 2D material-engineered meso-

scopic n–i–p architecture as an effective method to design and realize PSMs. In particular, graphene-based ETLs are exploited to accelerate the electron extraction/collection, as well as to control the perovskite morphology over the mesoscopic scaffold. Furthermore, chemically functionalized molybdenum disulfide (fMoS₂) is used as an efficient ABL at the perovskite/HTL interface for improving the hole injection/collection at the counter-electrode (CE). A thermal-assisted spray coating technique is exploited to deposit fMoS₂ ABL without damaging the underlying perovskite film. Our 2D material-engineered PSMs have shown a PCE of 13.4% and 15.3% on active areas of 108 cm² and 82 cm², respectively. Moreover, the use of 2D materials allows the PSMs to achieve a satisfactory lifetime, displaying a PCE retention of 75%, under prolonged thermal stress at 65 °C (ISOS-D2) over the first 1000 h,

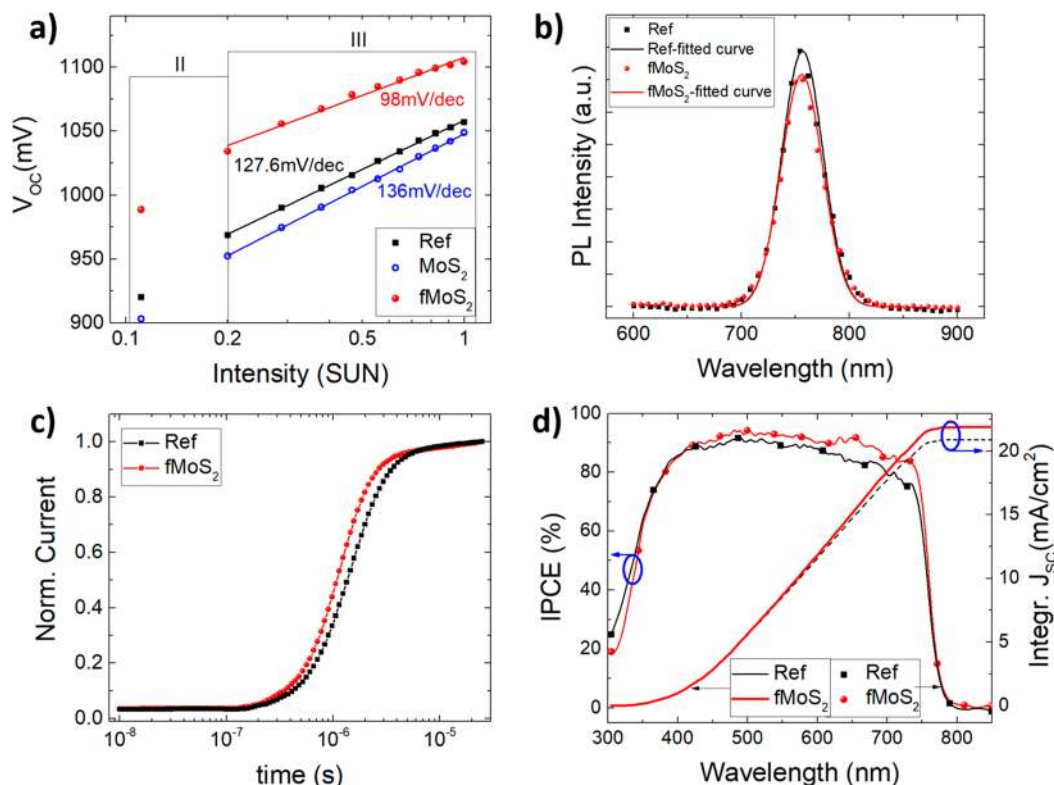


Figure 3. Transient and electro-optical analysis on as-produced PSCs. (a) V_{OC} vs $\log(P_{inc})$ plot for the different devices with and without ABLs. (b) Photoluminescence (PL) emission from the devices without Au CE. (c) Transient photocurrent profile acquired by switching on the LED light for $fMoS_2$ -based and reference devices. (d) Incident-photon-to-current conversion efficiency (IPCE) spectra and the corresponding integrated J_{sc} for $fMoS_2$ -based and reference devices. All the measurements in (c) and (d) are acquired on complete devices.

198 confirming the crucial role of 2D material-based layers in
199 preventing perovskite/CTL interface degradation.

200 *Small-Area Devices.* The proposed 2D material-engineered
201 PSC architecture is depicted in Figure 1a, the following are the
202 details: glass/FTO/ $cTiO_2+G$ / $mTiO_2+G$ /perovskite/spiro-
203 OMeTAD/ MoS_2 or $fMoS_2$ /Au. The graphene-doped $cTiO_2$
204 ($cTiO_2+G$) layer was deposited by the same spray pyrolysis
205 protocol from the $cTiO_2$ dispersion doped with graphene ink
206 (1 vol %) dispersed in a mix of ethanol and water (80:20, v/v),
207 while $fMoS_2$ (dispersed in 2-propanol) ABL was uniformly
208 sprayed on large-area substrates by a thermal-assisted spray
209 coating technique. More in detail, during the spray deposition,
210 the module substrates were kept at 80 °C to speed up the
211 evaporation of the $fMoS_2$ ink solvent and to prevent the
212 perovskite degradation, in agreement with protocols previously
213 reported.³⁰ The experimental details regarding the device
214 manufacturing and the characterization tools used for device
215 analysis are reported in the Supporting Information.

216 In particular, the prototypical ETL ($cTiO_2/mTiO_2$) was
217 modified by the addition of graphene flakes into both the
218 $cTiO_2$ ($cTiO_2+G$) and the $mTiO_2$ ($mTiO_2+G$). As reported in
219 our previous works,⁸³ the insertion of graphene flakes into the
220 $cTiO_2$ decreases the series resistance of the cell, which
221 consequently exhibits high fill factor, FF (typically >75%),
222 compared to the reference without graphene flakes.⁸⁴ Actually,
223 the graphene flakes provide effective electrically conductive
224 pathways to transport the electron toward the FTO electrode.
225 Alongside, the addition of the graphene flakes into the $mTiO_2$
226 improves the device PCE by increasing both the FF and short
227 circuit current (I_{sc}).⁵³ In agreement with steady-state
228 photoluminescence (PL) and time-resolved photolumines-

229 cence (TRPL) spectroscopy measurements, the perovskite
230 optimally crystallizes when it is wrapped into the $mTiO_2+G$,
231 enhancing the electron injection efficiency at the $mTiO_2+G$ /
232 perovskite interface.⁵⁵ Theoretical simulations have also
233 evidenced a ferroelectric distortion of the perovskite in contact
234 with graphene, which drives electron extraction from the
235 perovskite and hinders electron-hole recombination.⁸⁵ Mean-
236 while, the presence of graphene in the bare $mTiO_2$ layer
237 improves the overall electron transport toward the $cTiO_2$,
238 decreasing the series resistance and, thus, the FF of the
239 device.⁵⁵ As a further step for the realization of efficient PSCs,
240 an appropriate energy level tailoring at the perovskite/HTL
241 interface is pivotal to improve the hole extraction for the
242 perovskite to the HTL, eventually impeding the interface
243 degradation induced by charge trapping phenomena.⁵⁹ In this
244 context, several 2D material-based films, mainly transition
245 metal dichalcogenides (TMDs), have been proposed as
246 effective ABLs at the perovskite/HTL interface.^{59,86–88}
247 Among them, we exploited MoS_2 flakes, as obtained by liquid
248 phase exfoliation (LPE) of bulk crystals in 2-propanol (see
249 Supporting Information, Figure S1). The as-produced
250 dispersion can be deposited over perovskite as an ABL by
251 thermal-assisted spray coating (resulted by heating the
252 substrate at 80 °C).^{84,89} However, the MoS_2 valence band
253 edge does not perfectly match with the perovskite highest
254 occupied molecular orbital (HOMO) level and possibly forms
255 an energy barrier for the hole extraction process. To avoid this
256 drawback, we have also produced chemically functionalized
257 MoS_2 flakes ($fMoS_2$), by linking thiol of 3-mercaptopropionic
258 acid (MPA) moieties to the MoS_2 surface via S–S van der
259 Waals physisorption⁹⁰ and/or S-vacancy passivation.^{91,92}

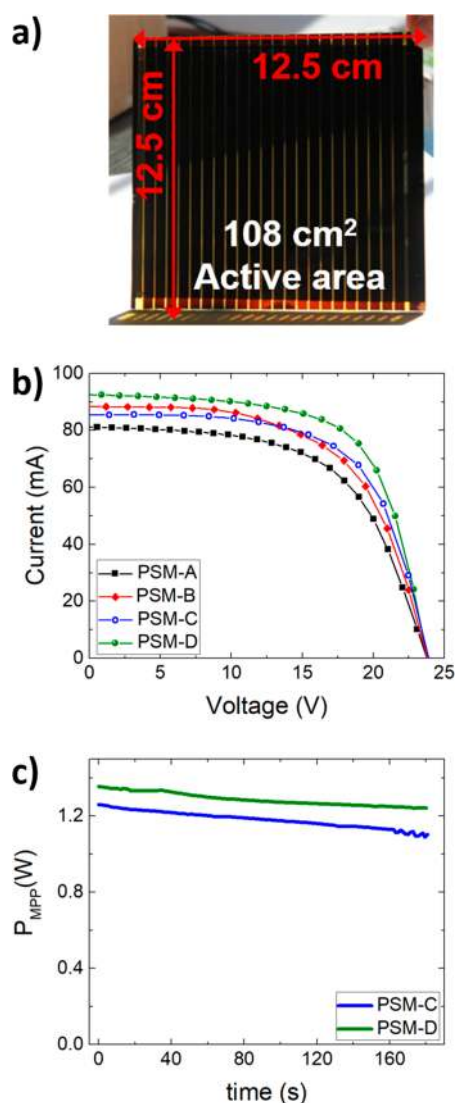


Figure 4. (a) Photograph of a representative large-area PSM (108 cm² active area, 156.25 cm² substrate area). (b) I - V characteristics of tested PSMs. (c) Stabilized power at maximum power point (P_{MPP}) under 1 sun illumination for PSM-C and PSM-D.

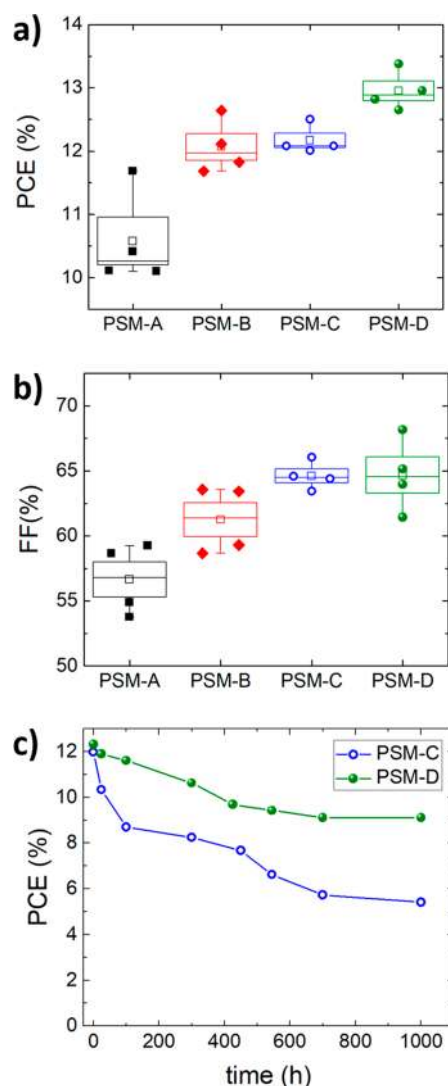


Figure 5. (a) PCE and (b) FF statistics for the various PSMs extracted by the corresponding I - V characteristics under 1 sun illumination. (c) PCE trends vs time extracted by the I - V characteristics under 1 sun illumination, periodically acquired during the prolonged thermal stress test at 65 °C (ISOS-D2) for PSM-C and PSM-D. The statistics were measured on four PSMs for each configuration.

260 Beyond chemically and electronically repairing the defective
 261 lattice of the MoS₂ flakes,⁹¹ the MPA-based functionalization is
 262 effective to shift MoS₂ energy bands up (see characterization
 263 measurements in Figure S2). Actually, MPA has also been
 264 recently exploited to shift the energy bands of PbS quantum
 265 dots up,⁹³ offering a versatile tool to engineering the interfaces
 266 in optoelectronic devices.⁸³ In our case, as sketched in Figure
 267 1b, the upshift of the MoS₂ energy bands has an immediate
 268 dual role: (1) to align the valence band edge of MoS₂ with the
 269 HOMO level of the perovskite, improving the hole extraction
 270 process,⁹³ and (2) to shift the conduction band edge of MoS₂
 271 above the LUMO level of the perovskite, restricting undesired
 272 electron transfer (i.e., providing electron blocking proper-
 273 ties).³⁰

274 To assess the beneficial role of fMoS₂ as ABL, small-area
 275 devices (0.09 cm² active area) were fabricated using graphene-
 276 based ETLs without (reference sample) and with MoS₂ or
 277 fMoS₂ ABLs at the perovskite/HTM interface. Figure 2 reports
 278 the photovoltaic parameter statistics for the various PSCs

279 extracted by the current-voltage (I - V) characteristics under 1
 280 sun illumination.

281 Clearly, the insertion of the ABLs increases the PCE of the
 282 PSCs compared to the reference architectures. More in detail,
 283 the PCE increase is larger for cells with fMoS₂ (+11.6%)
 284 compared to that of MoS₂ cells (+3.7%). In fact, although the
 285 average J_{SC} increases for both ABL-based architectures (+4.8%
 286 and +7.2% for MoS₂ and fMoS₂, respectively) compared to
 287 reference devices, the FF and the V_{OC} relatively increase only
 288 for fMoS₂-based devices (+2% and +1%, respectively).
 289 Compared to both reference and MoS₂-based cells, in
 290 fMoS₂-based devices, the increase of FF is attributed to a
 291 well-balanced hole and electron extraction, while the correct
 292 energy alignment between the perovskite HOMO and the
 293 fMoS₂ valence band edge explains the increase of the
 294 V_{OC} . Both these effects synergistically boost the PCE of the
 295 champion fMoS₂-based cell up to 19.2% (averaged PCE of
 296 18.3%).

297 The beneficial role of fMoS₂ into the device architecture was
298 confirmed by both electrical and spectroscopic measurements.
299 First, V_{OC} values were acquired by progressively increasing the
300 incident power (P_{inc}) with a calibrated white LED, as shown in
301 the V_{OC} vs log(P_{inc}) plot (Figure 3a). In fact, the analysis of the
302 latter allows the working mechanisms (i.e., charge generation/
303 recombination/collection) of PSCs to be studied.⁹⁴ In
304 particular, at low irradiance level (P_{inc} < 0.2 sun, region II)
305 the slope of the V_{OC} vs log(P_{inc}) plot is related to the electron
306 quasi-Fermi level, which is determined by the charge
307 accumulation and density of states in the ETL (i.e., cTiO₂ +
308 G/mTiO₂ + G).⁹⁴ Consequently, the devices show almost the
309 same V_{OC} slopes under such conditions. For larger P_{inc} (>0.2
310 sun, region III), the energy states of the ETL are fully filled,
311 and the charge generation and recombination rates within the
312 device determine the slope of the V_{OC} vs log(P_{inc}) plot.⁹⁴ In
313 particular, the slope increase (+7%) exhibited by the MoS₂-
314 based device compared to the reference cell is attributed to an
315 increase in the charge recombination rate at the perovskite/
316 HTM interface. In fact, the presence of MoS₂ can activate
317 additional recombination pathways compared to the bare
318 spiro-OMeTAD,⁸⁹ causing a slight decrease (−0.3%) of the
319 average V_{OC} (see Figure 2a). Interestingly, the devices using
320 the fMoS₂ ABL show the lowest slope (98 mV dec^{−1}) of the
321 V_{OC} vs log(P_{inc}) plot in region III (Figure 3a). This indicates
322 that the fMoS₂ ABL facilitates the hole transfer from the active
323 layer to the HTM compared to both reference and MoS₂-based
324 cells. Steady-state PL measurements were performed to further
325 evaluate the capability of the fMoS₂ ABLs to extract the
326 photogenerated holes from the perovskite. In fact, the hole-
327 extraction process hinders the radiative charge recombination
328 in the absorber material,^{95,96} which then shows a PL
329 quenching.⁹⁷ Figure 3b shows that the use of the fMoS₂
330 ABL reduces the PL emission of the perovskite. Quantitatively,
331 the PL decreases by 9% in the presence of fMoS₂ ABL
332 compared to the reference device. Thus, this result indicates
333 that fMoS₂ ABLs effectively accelerate the hole-extraction
334 dynamics at the photoelectrode. Transient photocurrent
335 measurements can be additionally carried out to reveal
336 information about the charge carrier transport within the
337 PSCs.⁹⁸ Figure 3c reports the transient photocurrent profile
338 recorded for both reference and fMoS₂-based devices. The data
339 show fast rises of the photocurrent (in the order of μs), which
340 are compatible with time scales associated with electron/hole
341 transport.^{99,100} Thus, the faster photocurrent rise in the case of
342 the fMoS₂-based device compared to the reference indicates
343 that the presence of the fMoS₂ ABL speeds up the hole charge
344 collection toward the CE of the devices. This improves the
345 charge collection efficiency, as also evidenced by incident-
346 photon-to-current conversion efficiency (IPCE) spectroscopy
347 measurements (Figure 3d). In particular, the integrated J_{SC} for
348 fMoS₂-based cells increases by 4.8% compared to those of
349 reference devices, in agreement with the J_{SC} values extrapolated
350 by the I–V characteristics under 1 sun illumination (Figure
351 2b). Overall, these data highlight the crucial role of the
352 functionalization of MoS₂ for optimal engineering of the
353 perovskite/ABL/HTM interface and increasing simultaneously
354 the J_{SC} and the V_{OC} relative to those of reference devices.
355 **Large-Area Modules.** The upscaling of PSCs toward PSMs
356 induces several performance losses, the most relevant ones
357 related to the interfacial charge recombination and the
358 interconnection of the multiple cells in a module.¹⁰¹ In fact,
359 on the one hand, it is critical to deposit the various PSM layers

over a large area with the same quality reached as in small-area
devices. Consequently, the interfacial charge recombination
experimentally increases with the increase of the interfacial
surface area. On the other hand, the typical PSM design
consists of a monolithic series interconnection of rectangular
subcells (with charge flowing across the smaller dimension),¹⁰²
since it effectively prevents an excessive increase of the series
resistance of the FTO contact (whose sheet resistance is in the
order of tens of Ω □^{−1}).¹⁰² However, the overall series
resistance given by the other layers of the subcells still causes
resistive losses, which decrease the FF and, thus, the power
output of the PSMs.¹⁰³ In this context, the performance losses
induced by the scaling-up process can be mitigated by the use
of a 2D material engineered structure investigated for small-
area devices, since it improves both the perovskite/CTL
interface and the conductivity of the ETL. Following this
rationale, the as-optimized mesoscopic PSCs were scaled up to
large-area PSMs. The reference module architecture (i.e.,
without 2D materials) is hereafter named PSM-A. The
structure based on the cTiO₂/mTiO₂+G layer and c-
TiO₂+G/TiO₂+G are named PSM-B and PSM-C, respectively,
while the fully optimized 2D material-engineered structure,
including the fMoS₂ ABL, is named PSM-D. The detailed
description of the PSM manufacturing is reported in the
Supporting Information. Briefly, the module production
requires several additional steps compared to that of small-
area devices. These steps consist of patterning the module cells
by four laser ablation processes.⁸³ In particular, a first laser
ablation step (P1) selectively removes the FTO to isolate
adjacent cells; a second laser ablation step (P2) removes the
complete ETL/perovskite/(ABL)/spiro-OMeTAD stack to
create the contact area between the cell vertical interconnec-
tion and the free FTO area. Lastly, a third ablation step (P3)
isolates the adjacent cells by removing the Au CE. For P2, the
power of a green laser (Nd:YVO₄, λ = 532 nm) was adjusted
carefully by evaluating the perovskite absorbance and the
eventual presence of 2D materials. First, PSM-C and PSM-D
with an active area of 82 cm² were produced over a 12.5 × 12.5
cm² substrate. Such PSMs were obtained by 10 series-
connected cells (single-cell active area of 8.2 cm²). As shown
in Figure S3 and Table S1, the as-produced fMoS₂-based
module (PSM-D) shows a PCE of 15.27%, representing an
improvement of 12.6% compared to the PCE of PSM-C
(13.56%). In fact, the fMoS₂ ABL in PSM-D increases the
module current (+3.9%) and FF (+8.3%) compared to PSM-
C. To further scale-up the PSM active area from 82 to 108 cm²,
the PSM layout was optimized in terms of cell width and dead
area between adjacent cells, leading to a final design consisting
of 22 series-connected cells with a single-cell active area of 4.9
cm² and a final aperture ratio (defined as AR = AA/(AA + DA)
in which AA is the active area and DA is the dead area) of 88%.
More in detail, in such a PSM layout, the P1, P2, and P3
scribes are 40, 30, and 30 μm, respectively, while the safety
area, i.e., the area between two adjacent laser scribes, is 135
μm. Figure 4a shows the photograph of an as-prepared large-
area PSM. The I–V characteristics of the champion devices for
each PSM are reported in Figure 4b, evidencing the best
photovoltaic performance for PSM-D, followed by PSM-C.
The stabilized powers at maximum power point (P_{MPP}) for
PSM-C and PSM-D are also reported in Figure 4c, indicating
that the use of the fMoS₂-based ABL increases the P_{MPP}
(+7.1%) compared to that of the PSM-C adopting the pristine
MoS₂-based ABL.

Figure 5a,b and Figure S4a,b report the photovoltaic parameter statistics for the various PSMs extracted by the I – V characteristics under 1 sun illumination. The PCE progressively increases passing from PSM-A to PSM-D (Figure 5a), confirming the crucial role of 2D material-based interface engineering for boosting the photovoltaic performance. In particular, the FF of the module (Figure 5b) undergoes an improvement of 14% passing from an average value of 57% to 65% for PSM-A and PSM-D, respectively. This improvement can be attributed to the effect of 2D material-based interface engineering, since all the investigated modules were realized adopting the same optimized layout. Moreover, the V_{OC} and the J_{SC} improved passing from PSM-C to PSM-D (+3.64% and +3.9%, respectively; see Figure S4), thus confirming the trend observed on small-area PSCs (see Figure 2a,b).

Notably, the fully 2D-material engineered modules (i.e., PSM-D, comprising both graphene-based ETLs and $fMoS_2$ -based ABLs) have shown an averaged PCE approaching 13%, with a record PCE of 13.4% and a record-high area-indexed aperture PCE ($AIAPCE = AA \times AR \times PCE$)⁸³ of 1266.5% cm^2 .

Finally, stability tests were performed by applying to the PSMs prolonged thermal stress at 65 °C in an oven (ISOS-D2)¹⁰⁴ and recording the corresponding PCE as a function of the thermal stress time (Figure 5c). The $fMoS_2$ -based module (PSM-D) exhibited a clear PCE stabilization, as evidenced by a remarkable improvement (+370 h) in the T_{80} lifetime (defined as the time span in which the device retains more than 80% of its initial efficiency) compared to the one of module PSM-C. Although a deeper investigation of the thermal-induced degradation mechanisms is still ongoing, we believe that the homogeneous $fMoS_2$ interlayer (as demonstrated in Figure S5) can be effective in (1) preventing the direct contact between the spiro-OMeTAD dopants and the perovskite surface, which promotes the interface degradation already experienced at 65 °C,¹⁰⁵ and (2) blocking atom migration from the Au electrode to the perovskite.⁶³

In conclusion, we have demonstrated 2D-material-engineered PSMs with a PCE of 13.4% over an active area of 108 cm^2 . This result, coupled with the superior thermal stability shown by 2D-based PSMs compared to reference devices, could pave the way for a feasible and reproducible scaling-up of perovskite-based photovoltaic technologies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b01151.

Details on employed materials, cell and module fabrication, material characterizations, electro-optical measurement setup (IPCE, ARKEO, I – V characteristics), and electrical characterization of the PSMs with both active areas of 82 cm^2 and 108 cm^2 (PDF)

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Author Contributions

A.A., S.P., and A.D.C. conceived the work. A.A., S.P., A.L.P., and A.D.C. performed the experiments on small and large area devices, the electro-optical characterizations, and the stress test. S.P. created the ToC/abstract graphic. L.N., S.B., B.M.G., I.M., and F.B. produced and characterized the 2D materials. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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