

Two-dimensional materials in perovskite solar cells

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Abstract

In the broad contest of halide perovskite solar cells (PSCs), interfaces play a meaningful role by ruling the efficiency and stability of devices. To decouple interface requirements from the bulk material properties, interface layers have been considered and successfully applied to improve solar cell performances. In this perspective, we analyze the use of two-dimensional (2D) materials such as graphene and related compounds as intra and inter layer in PSCs. A vast library of two-dimensional materials is nowadays available that allows for interface and work function engineering necessary for an effective optimization of solar cells. In addition, 2D materials can limit the ion diffusion, layer-by-layer degradation and moisture induce decomposition of perovskite, improving considerably the PSCs' stability. Their use is not only limited to lab-scale devices but it has been successful extended to large area perovskite modules, as well as to perovskite/silicon tandem cell, paving the way for an industrial exploitation of such 2D strategy.

Main Text

Modern electronic and optoelectronic devices are formed by a sequence of layers in a multimaterial/multijunction combination. Even Complementary Metal-Oxide Semiconductor (CMOS) technology, dominated for many decades by silicon and its native oxide SiO₂ is moving toward a multimaterial structure where germanium (for strain engineering), alternative oxides (for high dielectric constant insulators) and metal gates are efficiently combined with silicon. Owing to the increased number of (hetero)junctions in these multimaterial structures, a fundamental role is played by the interface between the different layers. Thus, it should not be a big surprise that also the halide perovskite (HP) photovoltaic features strongly rely on interfaces properties. In fact, a typical perovskite solar cell (PSC) is composed by an HP photon absorbing layer, sandwiched between selective charge transport layers (CTLs) and electrodes for negative and positive charge extraction. These materials are selected carefully by taking into account their compatibility with the underneath layers,¹ their charge mobility² and the energy level alignment with the perovskite absorber.³ Similarly to other multimaterial/multijunction devices, interfaces in PSCs play a crucial role in setting device performances and stability: charge transfer at the interfaces,⁴ interface band alignment,⁵ interfacial vacancies,⁶ defects due to poor adhesion between layers⁷ and energy barriers are all controlled by interfaces. However, HP are peculiar materials bridging the conventional semiconductor with ionic conductor. In fact, HP can be considered as crystalline liquid^{8,9} where the sublattice of organic cation liquid is confined in nanoscopic pore defined by the sublattice of corner-sharing PbX₆³⁻ (X = I, Br, or Cl) octahedral.¹⁰

The crystal-liquid duality has been discussed in relation with HP to explain the large polaron formation and screening of charge carriers, leading to defect tolerance, moderate charge carrier mobility, and radiative recombination properties.¹⁰ Beside these physical properties the existence of a "liquid" behavior is also manifested by the mobility of ions into the crystal structure caused by the migration of halide-ion vacancies V-X (X = I, Br, Cl).^{11,12} For this reason HP are considered solid-state mixed conducting materials where both electrons and ions contribute to the charge transport.¹² Halide ion migration, as well as organic/inorganic cation and Pb migrations,^{13,14} are shown to be related to hysteresis, giant capacitance and stability of devices.¹⁵ Besides these intrinsic species, also extrinsic ions coming from adjacent layers (Li⁺, Na⁺, OH⁻, H⁺

etc.) can migrate across the perovskite, impacting the device operation.¹⁶ The relation between solar cell degradation and ion migration has been addressed by several authors, however many of the reactions are reversible¹⁷ and ion migration will not induce degradation by per-se unless the ion is leaving the perovskite layer or the solar cells itself. In this respect the use of insulating interface layers such as poly(methyl methacrylate) (PMMA), polyethylene oxide (PEO), Polystyrene (PS) can prevent ion migration, passivate the defects of perovskite and, consequently, increase the stability of the cell.¹⁸

Another peculiar characteristic of HP used in solar cells is related to the architecture of the cell. In fact, together with classical thin film photovoltaic where a planar configuration of the different layer forming the cell is used,¹⁹ PSC can be in the form of mesoscopic structure where the HP absorber is nucleated into and above a mesoporous transporting layer, typically TiO₂.²⁰ Such n-i-p mesoporous configuration is very effective and was providing the most efficient PSCs. Here, an interface with larger equivalent surface between the mesoporous transporting layer and the perovskite is formed with respect to planar configuration and any interface instability could be easily enhanced.

Interface instability is typical in heterojunction devices and was, for example, one of main problem in the development of high-k silicon mosfets.²¹ Heterointerfaces are critical region of matching between two different material where electrical (charge transfer, interlayer resistance, defects, charge accumulation and recombination), chemical (miscibility, wettability, surface tension etc.), structural (strain, dislocation, defects) and mechanical (adhesion/delamination⁷), problems could arise. In HP devices this problem is further emphasized because of the possible presence of an organic/inorganic heterojunction typically fabricated at low temperature without a specific epitaxy.

Owing to the general problem of heterointerfaces and the specific characteristics of HP, a pivotal role of interface engineering (IE) has recently gained attention as a strategy to master the efficiency and stability performance of PSC.²² More in details, IE aims to improve the charge injection/collection at perovskite/CTLs interfaces by modifying the chemical/physical properties of involved layers at the interface. This is possible by inserting inter or buffer layers^{23,24} or simply by changing the composition and eventually the morphology of CTLs.²⁵

Interface layers offer an additional degree of freedom in the device design permitting to i) decouple the adjacent layers, ii) tune physical, chemical and structural interface properties without impacting on the material choice of the adjacent layers, iii) reduce the degradation avoiding cross contamination of the layers, iv) guide the epitaxial growth of two adjacent layers improving their structural properties. Several strategies have been developed so far to master interface properties by using small molecules, polymers, self-assembling monolayers, inorganic thin film, nanomaterials with both chemical and physical deposition techniques.²⁶

Among these approaches, the use of two-dimensional (2D) materials such as graphene and related materials (GRM) and transition metal dichalcogenide (TMD), has been proposed and demonstrated to be very effective. 2D materials have gained importance due to their unique physical and chemical properties such as tailored electrical conductivity, mechanical robustness, high optoelectronic tunability, easy production and solution processability.²⁷ A vast library of 2D materials exists with several thousand materials from metals to semiconductors and insulators that can be dispersed in several solvents and optimized for printing processes. Moreover, 2D materials can vary their properties if stacked with other 2D materials by generating novel material structures with new properties.²⁸ ²⁹Large amounts of 2D materials with unusual optoelectronic properties can be produced on-demand by liquid phase exfoliation or by ball-milling technique,³⁰ making their use suitable for large-scale industrial production. 2D materials could suffers from restacking, resulting from strong interlayer interaction and high surface energy. When this occurs, 2D materials can be functionalized with small molecules, metal nanoparticles, self-assembled monolayers, ionic liquids and polymers,³¹⁻³³ retaining the potential advantages offered by their 2D nature. This confers them wide processability in organic and polar solvent and/or the ability of patterning using photolithographic techniques. Nevertheless, Chemical Vapour Deposition techniques are also available for well controlled 2D materials making the possible fabrication choice quite large.

IE with 2D materials is one of the most promising strategy to boost both PCE and stability of PSC³⁴ and has been extended also to other devices based on HP.³⁵ One of the main potentialities of 2D materials is the possibility to easily tailor their electronic structure, such as Work Function (WF)³⁶ or band gap,³⁷ by operating a specific choice of the 2D material, by proper functionalization and eventually by inducing a quantum confinement playing with the lateral dimension of the 2D material.³⁸ Fine-tuning of WF and band gap allows to obtain appropriate energy level alignment leading to an ideal energy offset between perovskite active layer and CTLs, eventually inducing built-in potential for efficient charge collection at the electrodes. From the photovoltaic performance point of view, a good energy level alignment is paramount to achieving ideal open-circuit voltage (V_{oc}), by minimizing the carrier recombination losses and reducing the hysteretic behaviour of PSC. It also contributes to optimal charge extraction, leading to high short circuit current density (J_{sc}) and larger fill factor (FF). As an example, the possibility to chemically or thermally modify GRMs allows their oxygen vacancy/defect concentration to be changed, varying their optoelectronic properties.²⁷ This permits GRMs to be used as electron or hole transporting layers as well as interlayers at the perovskite/CTL interface.²²

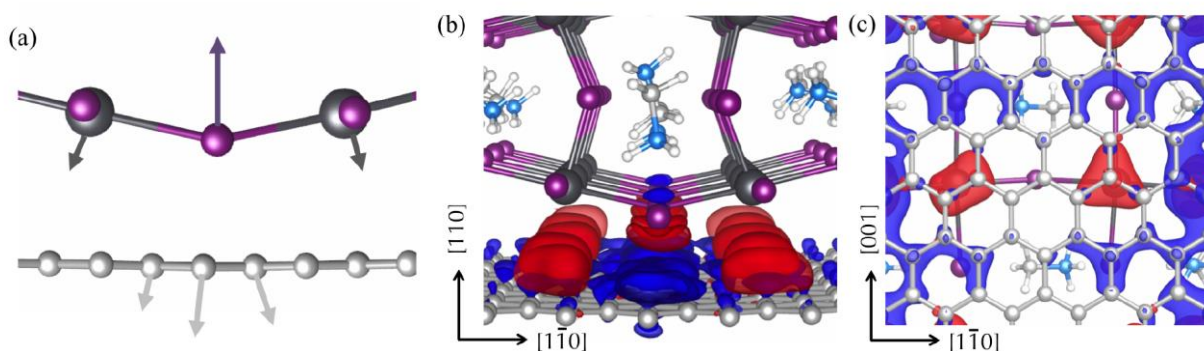


Figure 1: Atomistic modelling of the interface between MAPbI₃ and graphene. a) Forces acting on the atoms near the interface, leading to the suppression of the octahedral tilt in MAPbI₃. b,c) Electron charge rearrangement upon the formation of the interface between graphene and MAPbI₃. The red (blue) isosurface shows electron depletion (accumulation). Adapted with permission from Ref.³⁹

The synergy between HP and 2D materials has recently been revealed. A beneficial interaction between CH₃NH₃PbI₃ (MAPbI₃) HP and graphene has been outlined by the theoretical work of Volonakis and Giustino.^{39,40} DFT (Density Functional Theory) calculations shows that i) the interface between MAPbI₃ and graphene is stable, ii) the octahedral tilt of the MAPbI₃ is reduced pushing the I atoms away from the graphene while attracting the Pb atoms (**Figure 1**) and iii) the resulting interfacial potential step, of the order of 0.3 eV, is expected to assist electron transfer from MAPbI₃ to graphene, and to act as a barrier for photogenerated holes.^{39,40} The impact of graphene on the octahedral phase has been verified experimentally showing that transition between tetragonal to octahedral is inhibited by the presence of graphene.²⁵ An “healing effect” of graphene preventing carrier trapping near the surface of metal halide perovskites has been also theoretically demonstrated: when the surface of MAPbI₃ is covered with a graphene sheet, the presence of I, Pb and/or methylammonium (MA) vacancies is reduced and consequently the charge trap density reduces.⁴¹

The presence of graphene within the mesoporous layer can increase the device lifetime under different stress test conditions.⁴² In fact, graphene can locally reduce the light-induced perovskite degradation and the consequent release of iodine species, which diffuse across the interfaces and cause the modifications at the gold electrode (Au-I bonding) and the TiO₂ (Ti-I bonding) interfaces.⁴³ In addition, an improved stability of the carrier temperature was demonstrated when graphene is embedded in mesoscopic electron transporting layer, reflecting the superior stability of perovskite nanocrystals in the mesoporous region.⁴⁴

Such encouraging results pushed the scientific community to address new classes of 2D materials with optoelectronic properties customized for specific PSC structures and for specific interfaces. In this context, several efforts have been devoted to varying the WF of 2D materials to better match with the PSC interface requests.⁴⁵ Even though this strategy has been demonstrated to be compatible with PSC, the tunability of WF was quite restricted to values above 4eV, consequently limiting its applicability.⁴⁶

The use of GRMs and other 2D materials for a direct tuning of WF is not limited to CTLs but can be also extended directly to the perovskite. Mastering the perovskite WF without changing other properties such as band gap and optical absorption, is of paramount importance for band alignment with CTLs and consequently for the enhancement of charge transfer and reduce interface losses. Such approach has been recently demonstrated by employing a new class of 2D materials, namely the transition metal carbides, nitrides and carbonitrides (MXenes). MXenes, with a general formula $M_{n+1}X_nT_x$ ($n = 1, 2, 3$), where M represents an early transition metal, X is carbon and/or nitrogen, and T_x stands for surface terminations (such as OH, O, and F), came out as a promising class of 2D materials in particular for what concerns WF. During the synthesis of MXenes, their surfaces are naturally functionalized, which changes the electrostatic potential near the surfaces and affects the electronic structures, significantly shifting the WF.⁴⁷ As density functional theory predicts, surface termination strongly influences the density of states⁴⁸ and the WF of MXenes⁴⁹ which can range from 1.6 eV (for OH-termination) to 6.25 eV (for O-termination)⁴⁹. This opens new exciting opportunities for MXene applications in optoelectronics and photovoltaics. $Ti_3C_2T_x$ MXenes were incorporated into the perovskite absorber layer showing an improved morphology of the perovskite and an enhanced PCE with respect to the reference cell without MXenes (+12%).⁵⁰ In 2019, Yang and coworkers⁵¹ proposed $SnO_2-Ti_3C_2$ MXene nanocomposite as electron transport layers (ETLs) in low-temperature processed planar PSCs. The authors demonstrated the role of Ti_3C_2 MXene nanosheets in WF shifting of ETL providing superior charge transfer paths that permits to enhance the PCE of MXene-based PSCs with respect to the reference cells (+6.5%). $Ti_3C_2T_x$ MXene with various termination groups (T_x) has been used to engineer the perovskite/ETL interface and, when dispersed into the perovskite to tune the WF of the perovskite absorber.⁵² The combined action of WF tuning and IE can lead to substantial performance improvements in MXene-modified perovskite solar cells, as shown by the +26% increase of power conversion efficiency (that was above 20%) and hysteresis reduction with respect to reference cells without MXene. This finding has been supported by DFT calculation showing the large and non-linear variation of perovskite WF induced by MXenes with different termination groups.⁵² The MXene-PSC strategy has just begun, however, its impact on WF tuning and IE can inspire innovative efficient designs of PSCs and other perovskite-based devices such as light emitting diodes (LEDs) and detectors. Moreover, the proposed approach can be easily scaled-up to large area modules and panels, since the MXene doping involves only the precursor solutions and it does not impact the deposition method.

Figure 2 and Table 1 summarize the use of 2D materials in PSC showing the maximum efficiency reached so far by using a specific 2D material in a specific part of the cell. According to the scientific investigation, we consider the use of 2D material as interface layer in several parts of the cells, as a dopant for the layers, as a CTL replacing the bulk material and as electrode.

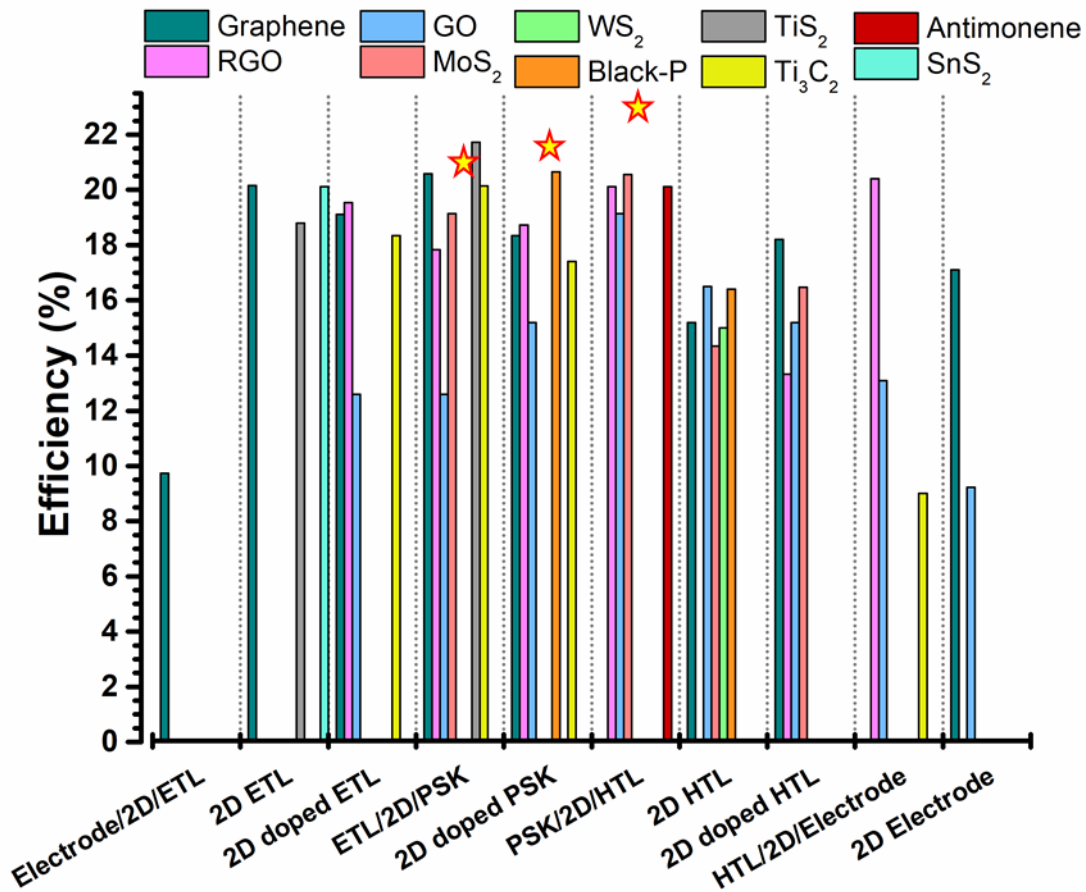


Figure 2. Maximum efficiency of PSC obtained by using 2D materials in specific part of the cells. Colors refer to the 2D materials used. Numerical data, perovskite formula and references are reported in Table 1. 2D perovskites (★) have been also used as interlayer at the perovskite/HTL and perovskite/ETL interface, as well as in the perovskite composition (2D/3D perovskite).

	G	RGO	GO	MoS ₂	WS ₂	Black-P	TiS ₂	Ti ₃ C ₂	Sb	SnS ₂	2D PSK
Contact /2D/ETL	MAPbI ₃ 9.73% [53]										
2D ETL	FA _{0.75} MA _{0.15} CS _{0.1} PbI _{2.65} Br _{0.35} 20.16% [54]						(FAPbI ₃) _{1-x} (MAPbBr ₃) _x 18.79% [55]	MAPbI ₃ 17.17% [56]		FA _{0.75} MA _{0.15} CS _{0.1} PbI _{2.65} Br _{0.35} 20.12% [57]	
2D doped ETL	MAPbI ₃ 19.11% [58]	(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} 19.54% [59]	MAPbI ₃ 12.6% [45]					MAPbI ₃ MAPbI ₃ 18.34% [51]			

ETL/2D/ PSK	MAPbI _{3-x} Cl _x :Ag- rGO 20.58% [60]	(FAPbI ₃) 0.85 (MAPbBr 3) _{0.15} 17.83% [61]	MAPbI ₃ 12.6% [62]	MAPbI ₃ 19.14% [63]			(FAPbI ₃) 0.85(MAP bBr ₃) _{0.15} 21.73% [64]	Cs _x (MA _{0.83}) 1- x)Pb(I _{0.83} Br _{0.17}) ₃ 20.14% [52]			MAPbI ₃ 20.9% [65]
2D doped PSK	MAPbI ₃ 18.34% [66]	FA _{0.85} MA 0.15Pb(I _{0.8} 5Br _{0.15}) ₃ 18.73% [67]	MAPbI ₃ /GO 15.2% [68]			MAPbI ₃ / BP 20.65% [69]		MAPbI ₃ / Ti ₃ C ₂ 17.41% [50]			FAMAPb I ₃ 21.49% [70]
PSK/2D /HTL		MAPbI ₃ 20.12% [37]	MAPbI ₃ 19.14% [63]	MAPbI ₃ 20.55% [71]					MAPbI ₃ 20.11 % [72]		(FAPbI ₃) 0.95(MAP bBr ₃) _{0.05} 23% [73]
2D HTL	MAPbI ₃ 15.2% [74]		MAPbI ₃ 16.5% [75]	MAPbI ₃ 14.35% [76]	MAPbI ₃ 15% [76]	MAPbI ₃ 16.4% [77]					
2D doped HTL	(NH ₄ CH ₃ N H ₃) _{0.3} (N H ₃ CH ₃) _{0.7} PbI ₃ (FA _{0.3} MA _{0.7} PbI ₃) 18.2% [78]	MAPbI ₃ 13.33% [79]	MAPbI ₃ 15.2% [68]	MAPbI ₃ 16.47% [80]							
HTL/2D /Contac t		CsFAMA PbI _{3-x} Br _x 20.4% [24]	MAPbI ₃ 13.1% [81]					CsPbBr ₃ 9.01% [82]			
2D Electrod e	MAPbI ₃ 17.1% [83]		MAPbI ₃ 9.23% [84]								

Table 1. Numerical value of maximum efficiency of PSC obtained by using 2D materials in specific part of the cells (as for Fig. 2). References to the paper where the work is performed are reported.

So far, the most efficient PSC exploiting the properties of 2D materials has been obtained by using TiS₂ as interlayer between the SnO₂ ETL and the multication HP, achieving a PCE=21.73%. The improvement of the device performance was attributed to two aspects, namely i) a better alignment of energy levels due to TiS₂ interlayer and ii) the passivation of the trap states. This result is very promising showing that the emerging 2D materials could improve further the efficiency of PSC. We should point out that results of Fig.2 and Table 1 refer to single junction PSCs. However, the tailoring of electronic/optical properties with 2D materials can be extended to tandem junction such as HP/silicon solar cells. In this context, graphene has been used as contact layer exploiting its good conduction and transparency properties⁸⁵ as well as dopant of TiO₂ ETL in mechanically stacked two-terminal tandem cell able to push the efficiency up to 26.3%.⁸⁶

Besides improving of efficiency, 2D materials have been shown to be extremely effective for stability of HP. The main observation came by the seminal work of Z. Fan and co-workers⁸⁷ showing that the thermal degradation (85 °C) of MAPbI₃ crystalline structure shows a gradual evolution from tetragonal MAPbI₃ to trigonal lead iodide layered crystals with a fixed crystallographic direction. The degradation starts at the surface of MAPbI₃ and progresses in a layer-by-layer fashion (See **Fig. 3**). To prevent this degradation, the same authors proposed to protect the HP surface with a 2D material, namely h-BN. They showed that h-BN/HP/h-BN stack does not show structural change after 30 min of continuous heating at 85°C, in stark contrast to the rapid emergence of the trigonal phase within 1 min and the complete transformation to trigonal PbI₂ within 7 min of the same thermal treatment for the non-encapsulated HP. Following this discovery, BN has been used to prevent degradation of inorganic HP (CsPbI₃) laser devices.⁸⁸

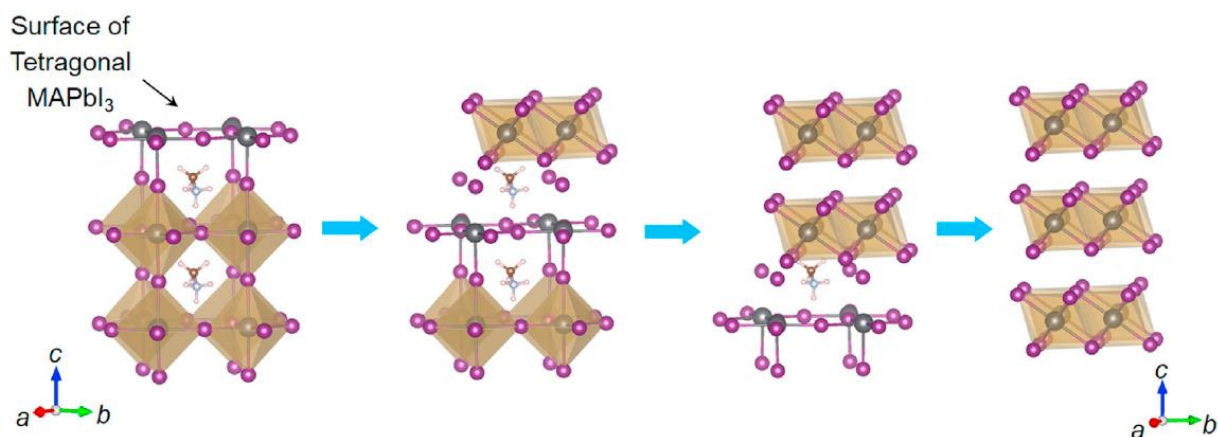


Figure 3. Schematic illustration of the layer-by-layer degradation of MAPbI₃ to produce the stacked trigonal/tetragonal structure with preserved crystallographic orientation. The surface of tetragonal MAPbI₃ is transitioning one by one to PbI₂ layers, exposing the underlying layer as the new surface layer as degradation progresses. Adapted with permission from Ref. ⁸⁷

Beside the surface morphology protection, 2D materials are also very effective to prevent ion migration.¹⁴ To clarify this role, Rand and co-worker interfaced 2D single crystal perovskite with a graphene layer in a field-effect transistor (FET) configuration.⁸⁹ They revealed that iodide loss is an important degradation pathway of 2D perovskite single crystals which can be suppressed by covering perovskites with graphene, thus significantly improving 2D perovskite stability.

The ability of 2D material to prevent the ion diffusion and the reaction between adjacent layer has been exploited by Graetzel group in one of the most successful attempt to improve the stability of mesoscopic PSC.⁹⁰ Here, the operational stability (light soaking at maximum power point and temperature equal to 60 °C) of a mesoscopic PSC with Copper thiocyanate (CuSCN) as Hole transporting Layer (HTL) and Au as top electrode was increased from few hours till 1000 hours by placing Reduced Graphene Oxide (RGO) interlayer between CuSCN and Au (**Figure 4**).

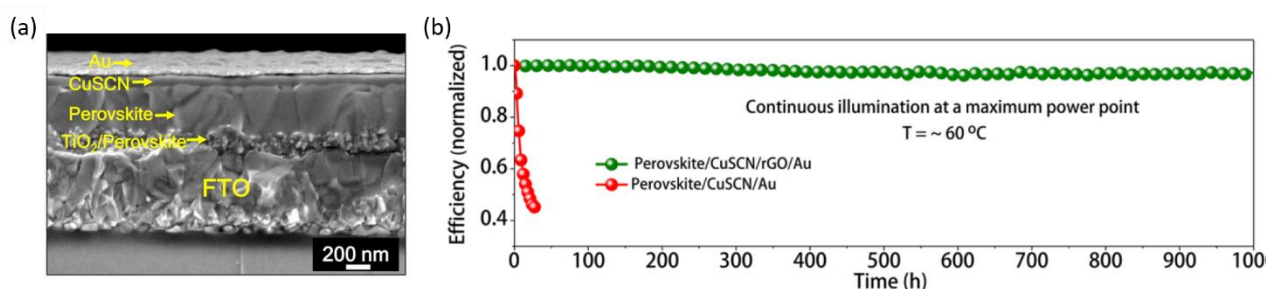


Figure 4. Operational stability of an unencapsulated CuSCN-based device with and without a thin layer of rGO (as a spacer layer between CuSCN and gold layers), examined at a maximum power point under continuous full-sun illumination at 60°C in a nitrogen atmosphere. Adapted with permission from Ref.⁹⁰

MoS₂ was also used to improve the operational stability of inverted PSC beyond the state of art.⁹¹ The photovoltaic performances of the HTL/MoS₂/PSK/ETL retained 80% of their initial performance after 568 h of continuous stress test under 1 SUN light and at MPP in ambient conditions.

Regarding inverted PSCs, a two-fold approach has been recently implemented by using ultra-thin Bi₂Te₃ flakes to dope the ETL and to form, at the same time, a protective interlayer above the ETL. Bi₂Te₃-based PSCs reached a PCE up to 19.46% and retained more than 80% of their initial PCE, after a burn-in phase, over 1100 h under continuous 1 Sun illumination.⁹²

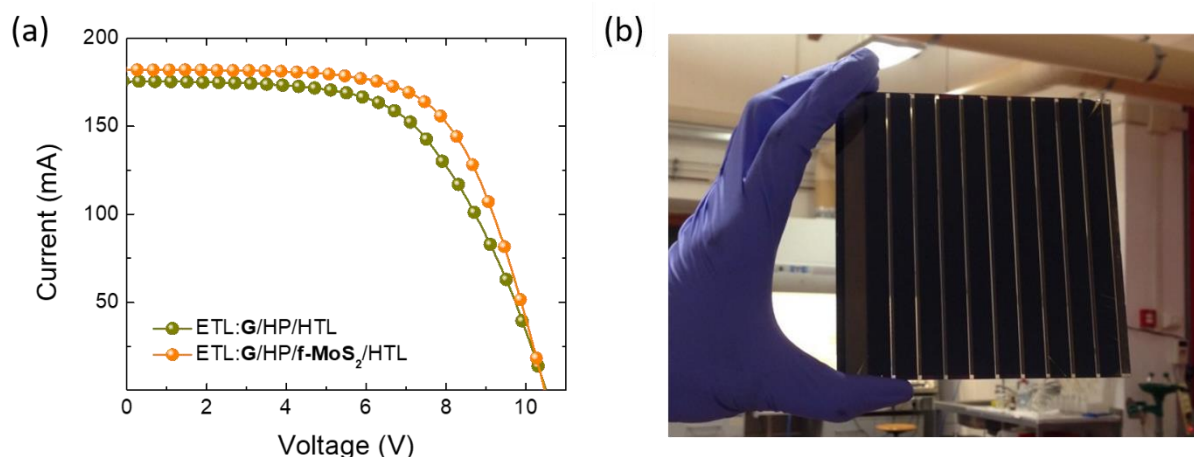


Figure 5. a) I–V characteristics of modules with Graphene into the TiO₂ ETL and with or without functionalized MoS₂ (f-MoS₂) at the interface between Perovskite and HTL. The module is realized on a 12.5 x 12.5 cm² substrate with an active area 82 cm². The efficiency on active area is 15.3%. b) image of the module. Details on module fabrication are reported in Ref.⁹³

Recently, 2D organic–inorganic halide perovskites have been attracting considerable attention because of their unique performance and enhanced stability for photovoltaic solar cells,⁹⁴ photoluminescent devices^{95,96} and photodetector.⁹⁷ The layered 2D perovskites show a wide tunability of optoelectronic properties⁹⁸ both from chemical and physical point of view.⁹⁹ In fact, the band gap can be systematically tuned from the UV to the near-infrared region even by controlling the nanoscale quantum confinement. Moreover, the 2D halide perovskites are direct band gap semiconductors regardless of the thickness and the number of metal halide octahedral layers between the two layers of the larger cations (mostly large size or long chain organic molecules). Lastly, the 2D perovskite showed increased stability that has been attributed to stronger van der Waals interaction between the capping organic molecules and the [PbI₆] unit, since the organic molecules are more strongly bound to the 2D perovskite than their MAI based 3D-structured counterpart. In addition, the longer alkyl chain of bulkier organic component ensures higher perovskite hydrophobicity when compared to the MA⁺ ions by improving the moisture stability.¹⁰⁰ Although the first generation 2D PSCs have shown relatively lower photovoltaic performance¹⁰¹, recent reports suggest that they are also capable of achieving high power conversion efficiency well beyond 20%.¹⁰² In this context, a synthetic protocol using Butylammonium (BA) as spacer has been developed in order to achieving the layered perovskites in the pure form, with a reduced number of layers, named 2D/quasi-2D perovskite. A record PCE of 18.2% was reported for 2D perovskites employing a BA-derivative as spacer cations,¹⁰³ while the unencapsulated devices sustain over 82% of their initial efficiency after 2400 h under relative humidity of ≈40%. The robust performance of perovskite solar cells results from the quasi-2D perovskite films was demonstrated to be related to the hydrophobic nature, the high degree of electronic order and high crystallinity.

Mixed composite of 3D and 2D perovskite phases, known as 2D/3D perovskites emerged as a class of excellent photovoltaic material with long-term stability. The 2D / 3D multi-dimensional perovskite interface revealed a bright example of IE by increasing the efficiency and stability of perovskite photovoltaics. In fact, the 2D layer acts as a protective interlayer preserving the efficient 3D perovskite from degradation. 2D perovskite has been included in an effective way in the 3D perovskite composition (2D/3D perovskite)⁷⁰ as well at the interface with HTL¹⁰⁴ and ETL⁷³ with efficiencies well exceeding 20% and extended operational stability under continuous light soaking (1-SUN) with respect to 3D perovskite. Grancini et al. demonstrated the unique combination of 2D/3D perovskite with a carbon-based architecture resulting in a large area modules able to sustain a continuous light-soaking for 10,000 hours without degradation of PCE.¹⁰⁵

The scaling-up of the perovskite PV technology, together with high efficiency, low production costs and long-term operational stability, is one of the main challenges to push perovskite solar cell toward industrial levels. A successful scaling-up from laboratory scale cells to large area modules and panels accounts for a uniformly

coat compact perovskite absorber (no pinholes), good grain morphology and optimized interfaces between adjacent layers. In fact, it is imperative to develop scalable fabrication processes capable of retaining the ability of nucleation and subsequently crystal growth processes.

The impact of 2D materials on efficiency and stability of PSCs and the ability to adopt conventional HP printing processes for the deposition of such 2D materials has been shown to be valid also for large area devices such HP solar modules.⁶² Recently, graphene and functionalized MoS₂ has been used for engineer both interfaces between HP and electrodes in large area modules, achieving PCEs of 13.4% and 15.3% on active areas of 108 cm² and 82 cm², respectively (Fig. 5). These modules showed a remarkable stability under prolonged (>1000 h) thermal stress test at 65°C (ISOS-D2), representing a crucial advancement in the exploitation of perovskite photovoltaic technology.⁹³ Notably, the proposed graphene IE strategy coupled with the use of stable polymeric hole transporting layer, allowed to realize perovskite large area module (active area >80cm²) complying with prolonged 80°C thermal stress as requested by standard ISOS D2 protocol.¹⁰⁶

Conclusions

Two-dimensional materials ranging from graphene to transition metal dichalcogenides and MXenes, including also 2D halide perovskites, have been demonstrated to be very effective in mastering efficiency and stability of perovskite solar cells and modules. 2D materials used as interface layers or dopant improve charge transfer, increase mobility, improve band alignment, tune work-function and limit ion diffusion. The beneficial role of 2D materials on efficiency and stability coupled to the availability of a wide library of 2D material and to the possibility to adopt conventional large area printing processes represent the hint for the development of a stable perovskite photovoltaic technology and to reduce the time to the market of perovskite solar cell technology. Moreover, some 2D materials have proven to be successful in replacing transporting layer and electrodes. This, combined with the recent development of high absorbing 2D halide perovskite and the realization of semi-transparent 2D electrodes based on GRM could pave the way for a full 2D photovoltaics.¹⁰⁷

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