Two-dimensional materials in perovskite solar cells

Aldo Di Carlo1,2, Antonio Agresti3, Francesca Brunetti4 and Sara Pescetelli4

1 Istituto di Struttura della Materia, CNR-ISM, via del fosso del cavalieri 100, 00133, Roma, Italy
2 CHOSE, Centre for Hybrid and Organic Solar Cells, University of Rome Tor Vergata, via del Politecnico 1, 00133, Roma, Italy
3 Author to whom any correspondence should be addressed.

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 mobility [2], 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 layers [7] 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 PbX6− (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’ behaviour 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 reversible [17] 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/delamination [7]), 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, 29]. Large 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 suffer 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 PSC [34] 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].

The synergy between HP and 2D materials has recently been revealed. A beneficial interaction between CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) 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 MAPbI$_3$ and graphene is stable, (ii) the octahedral tilt of the MAPbI$_3$ 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 MAPbI$_3$ 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 MAPbI$_3$ 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 4 eV, 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 states [48] and the WF of MXenes [49] 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. Ti3C2Tx 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 coworkers [51] proposed SnO2-Ti3C2 MXene nanocomposite as electron transport layers (ETLs) in low-temperature processed planar PSCs. The authors demonstrated the role of Ti3C2 MXene nanosheets in WF shifting of ETL providing superior charge transfer paths that permits to enhance the PCE of MXene-based PSC with respect to the reference cells (+6.5%). Ti3C2Tx 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.

So far, the most efficient PSC exploiting the properties of 2D materials has been obtained by using TiS$_2$ as interlayer between the SnO$_2$ 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 TiS$_2$ 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 figure 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 use as contact layer exploiting its good conduction and transparency properties [85] as well as dopant of TiO$_2$ 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-workers [87] showing that the thermal degradation (85 °C) of MAPbI$_3$ crystalline structure shows a gradual evolution from tetragonal MAPbI$_3$ to trigonal lead iodide layered crystals with a fixed crystallographic direction. The degradation starts at the surface of MAPbI$_3$ and progresses in a layer-by-layer fashion (see figure 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 PbI$_2$ 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 (CsPbI$_3$) laser devices [88].

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

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

| Contact/2D/ETL | G       | RGO     | GO       | MoS2 | WS2 | Black-P | TiS2 | TiI2C2 | Sb       | SnS2 | 2D PSK |
|----------------|---------|---------|----------|------|-----|---------|------|--------|----------|------|--------|
| 2D ETL         | MAPbI3  | 9.73% [53] |          |      |     |         |      |        |          |      |        |
|                | FA0.75MA0.25 | C80.1PbI2.65 | B70.22 20.16% |      |     |         |      |        |          |      |        |
| 2D doped ETL   | MAPbI3  | 19.11% [58] | (FAPbI3)0.85 | MAPbI3 | 12.6% | MAPbI3 | (MAPbBr)0.05 | MAPbI3 | 19.14% [63] |        |        |
|                | Ag-rGO  | 19.54% [59] | (MAPbBr)0.35 | MAPbI3 | 12.6% | MAPbI3 | (MAPbBr)0.15 | MAPbI3 | 19.14% [63] |        |        |
| ETL/2D/PSK     | MAPbI3,Cl: | 20.58% [60] | (FAPbI3)0.85 | MAPbI3 | 12.6% | MAPbI3 | (MAPbBr)0.35 | MAPbI3 | 20.14% [52] |        |        |
|                | MAPbI3,Cl: | 20.58% [60] | (FAPbI3)0.85 | MAPbI3 | 12.6% | MAPbI3 | (MAPbBr)0.35 | MAPbI3 | 20.14% [52] |        |        |
| 2D doped PSK   | MAPbI3  | 18.34% [66] | FA0.85MA0.15 | MAPbI3 | 20.65% | MAPbI3 | (FA0.85MA0.15)BP | MAPbI3 | 19.14% [63] |        |        |
|                | Pb(l0.3Br0.7) | 18.73% [67] | MAPbI3 | 20.65% | MAPbI3 | (FA0.85MA0.15)BP | MAPbI3 | 19.14% [63] |        |        |
| PSK/2D/HTL     | MAPbI3  | 20.12% [37] | MAI0.85 | MAPbI3 | 20.55% | MAPbI3 | (FAPbI3)0.85 | MAPbI3 | 20.11% [72] |        |        |
| 2D HTL         | MAPbI3  | 15.2% [74] | MAPbI3  | 15.2% | MAPbI3 | 15.2% | MAPbI3 | 15.2% | MAPbI3 | 23% [73] |        |
| 2D doped HTL   | MAPbI3  | 13.33% [79] | (NH4)2(Br)0.7 | MAPbI3 | 15.2% | MAPbI3 | (NH4)2(Br)0.7 | MAPbI3 | 15.2% |        |        |
|                | MAPbI3  | 13.33% [79] | (NH4)2(Br)0.7 | MAPbI3 | 15.2% | MAPbI3 | (NH4)2(Br)0.7 | MAPbI3 | 15.2% |        |        |
| HTL/2/Contact  | MAPbI3  | 18.2% [78] | (FAPbI3)0.85 | MAPbI3 | 15.2% | MAPbI3 | (FAPbI3)0.85 | MAPbI3 | 15.2% |        |        |
| 2D Electrode   | MAPbI3  | 17.1% [83] | CSFAMAPbI3 | MAPbI3 | 13.1% | MAPbI3 | (FAPbI3)0.85 | MAPbI3 | 13.1% |        |        |
|                | MAPbI3  | 17.1% [83] | CSFAMAPbI3 | MAPbI3 | 13.1% | MAPbI3 | (FAPbI3)0.85 | MAPbI3 | 13.1% |        |        |
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 h by placing Reduced Graphene Oxide (RGO) interlayer between CuSCN and Au (figure 4).

MoS$_2$ was also used to improve the operational stability of inverted PSC beyond the state of art [91]. The photovoltaic performances of the HTL/MoS$_2$/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 Bi$_2$Te$_3$ flakes to dope the ETL and to form, at the same time, a protective interlayer above the ETL. Bi$_2$Te$_3$-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].

Recently, 2D organic–inorganic halide perovskites have been attracting considerable attention because of their unique performance and enhanced stability for photovoltaic solar cells [93], photoluminescent devices [94, 95] and photodetector [96]. The layered 2D perovskites show a wide tunability of optoelectronic properties [97] both from chemical and physical point of view [98]. 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 [PbI$_6$]$_n$ unit, since the organic molecule 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 [99].
Although the first generation 2D PSCs have shown relatively lower photovoltaic performance \[100\], recent reports suggest that they are also capable of achieving high power conversion efficiency well beyond 20% \[101\]. 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 layer, named 2D/quasi-2D perovskite. A record PCE of 18.2% was reported for 2D perovskites employing a BA-derivative as spacer cations \[102\], while the unencapsulated devices sustain over 82% of their initial efficiency after 2400 h under relative humidity of \(\approx 40\%\). 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 form 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 HTL \[103\] and ETL \[73\] 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 h without degradation of PCE \[104\].

The scaling-up of the perovskite PV technology, together with high efficiency, low production costs and long-term operational stability, is one 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 MoS\(_2\) has been used for engineer both interfaces between HP and electrodes in large aera modules, achieving PCEs of 13.4% and 15.3% on active areas of 108 cm\(^2\) and 82 cm\(^2\), respectively (figure 5). These modules showed a remarkable stability under prolonged (>1000h) thermal stress test at 65 °C (ISOS-D2), representing a crucial advancement in the exploitation of perovskite photovoltaic technology \[105\]. 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 >80cm\(^2\)) 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].

Acknowledgments

We gratefully acknowledge the funding from the European Union’s Horizon 2020 research and innovation programme under Grant Agreement No. 696656 (GrapheneCore1), Grant Agreement No. 785219—GrapheneCore2 and Spearhead Project 3 ‘Graphene-perovskite solar farm’ during the Core2 project, grant agreement SGA 881603 GrapheneCore3 and Spearhead Project 5 ‘GRAPES’ during the Core3 project.

References

[1] Isabelli F, Di Giacomo F, Gorter H, Brunetti F, Groen P, Andriessen R and Galagan Y 2018 Solvent systems for industrial-scale processing of spiro-OMeTAD hole transport layer in perovskite solar cells ACS Appl. Energy Mater. 1 6056–63
[2] Wang Z K and Liao L S 2018 Doped charge-transporting layers in planar perovskite solar cells Adv. Opt. Mater. 6 1800276
[3] Courtier N E, Cave J M, Foster J M, Walker A B and Richardson G 2019 How transport layer properties affect perovskite solar cell performance: insights from a coupled charge transport/ion migration model Energy Environ. Sci. 12 396–409
[4] Fakhrauddin A, Schmidt-Mende L, Garcia-Belmonte G, Jose R and Mora-Sero I 2017 Interfaces in perovskite solar cells Adv. Electron. Mater. 7 2472–86
[5] Wang S, Sakurai T, Wen W and Qi Y 2018 Energy level alignment at interfaces in metal halide perovskite solar cells Adv. Mater. Interfaces 5 1800260
[6] Saitdinov M I et al 2018 Suppression of atomic vacancies via incorporation of isovalent small ions to increase the stability of halide perovskite solar cells in ambient air Nat. Energy 3 648–54
[7] Lee I, Yun J H, Son H J and Kim T S 2017 Accelerated degradation due to weakened adhesion from Li-TFSI additives in perovskite solar cells ACS Appl. Mater. Interfaces 9 7029–35
[8] Zhu H, Miyata K, Fu Y, Wang J and Josh P P 2016 Screening in crystalline liquids protects energetic carriers in hybrid perovskites Science 353 1409
[9] Kambhampti P 2019 Two-dimensional electronic spectroscopy reveals liquid-like lineshape dynamics in CsPbI3 perovskite nanocrystals Nat. Commun. 10 4962
[10] Miyata K, Atallah T L and Zhu X 2017 Lead halide perovskites: crystal-liquid duality, phonon glass electron crystals, and large polaron formation Science 361 1701469
[11] Mizusaki J, Ara K and Fueki K 1983 Ionic conduction of the perovskite-type halides Solid State Ionics 11 203–11
[12] Senocrate A and Maier J 2019 Solid-state ionics of hybrid halide perovskites J. Am. Chem. Soc. 141 8382–96
[13] Divitini G, Cacovich S, Matteocci F, Di Carlo A and Ducti C 2016 In situ observation of heat-induced degradation of perovskite solar cells Nat. Energy 1 15012
[14] Busby Y, Agresti A, Pescetelli S, Di A, Noel C, Pireaux J and Housiaux I. 2018 Aging effects in interface-engineered perovskite solar cells with 2D nanomaterials: a depth pro Fi Le analysis Mater. Today Energy
[15] Zhang T, Hu C and Yang S 2019 Ion migration: a ‘double-edged sword’ for halide-perovskite-based electronic devices Small Methods 4 1900552
[16] Li Z et al 2017 Extrinsic ion migration in perovskite solar cells Energy Environ. Sci. 10 1234–42
[17] Yamilova O R, Danilov A V, Mangruklar M, Fedotov Y S, Luchkin S Y, Babenko S D, Bredikhin S I, Aldoshin S M, Stevenson K J and Troshin P A 2020 Reduction of methylammonium cations as a major electrochemical degradation pathway in MAPI3 perovskite solar cells J. Phys. Chem. Lett. 11 221
[18] Kim M, Motti S G, Sorrentino R and Petrozza A 2018 Enhanced solar cells stability by hygroscopic polymer passivation of metal halide perovskite thin film Energy Environ. Sci. 11 2699–19
[19] Zheng X et al 2020 Managing grains and interfaces via ligand anchoring enables 22.3%-efficiency inverted perovskite solar cells Nat. Energy 5 131–40
[20] Park N-G 2019 Research direction toward scalable, stable, and high efficiency perovskite solar cells Adv. Energy Mater. 10 1903010
[21] Robertson J and Wallace R M 2015 High-K materials and metal gates for CMOS applications Mater. Sci. Eng. R 88 1–41
[22] Petridis C, Kakavelakis G and Kymakis E 2018 Renaissance of graphene-related materials in photovoltaics due to the emergence of metal halide perovskite solar cells Energy Environ. Sci. 11 1030–61
[23] Agresti A, Pescetelli S, Cinà I, Konios D, Kakavelakis G, Kymakis E and Di Carlo A 2016 Efficiency and stability enhancement in perovskite solar cells by inserting lithium-neutralized graphene oxide as electron transporting layer Adv. Funct. Mater. 26 2686–94
[24] Arora N, Dar M I, Hindertofer A, Pellet N, Schreiber F, Zakeeruddin S M and Grätzel M 2017 Perovskite solar cells with CsSCN hole extraction layers yield stabilized efficiencies greater than 20% Science 358 768–71
[25] Biccari F et al 2017 Graphene-based electron transport layers in perovskite solar cells: a step-up for an efficient carrier collection Adv. Energy Mater. 7 1701349
[26] Shao S and Loi M A 2019 The role of the interfaces in perovskite solar cells Adv. Mater. Interfaces 7 1901469
[27] Cai X, Luo Y, Liu B and Cheng H M 2018 Preparation of 2D material dispersions and their applications Chem. Soc. Rev. 47 6224–66
[28] Nourbakhsh, A, Yu L, Lin Y, Hempel M, Shiue R-J, Englund D and Palacios D 2019 Beyond-CMOS Technologies for Next Generation Computer Design (Berlin: Springer) pp 43–84

[29] Kang S, Lee D, Kim J, Capasso A, Kang H S and Park J 2020 2D semiconducting materials for electronic and optoelectronic applications: potential and challenge 2D Mater. 7 022003

[30] Han C, Zhang Y, Gao P, Chen S, Liu X, Mi Y, Zhang J, Ma Y, Jiang W and Chang J 2017 High-yield production of MoS2 and WS2 quantum sheets from their bulk materials Nano Lett. 17 7767–72

[31] Snapp P, Kim J M, Cho C and Leem J 2020 Interaction of 2D materials with liquids: wettability, electrochemical properties, friction, and emerging directions NPJ Sci. Mater. 12 22

[32] Yang S, Sato K, Suzuki J, Imai H and Oaki Y 2019 Amorphous 2D materials containing a conjugated-polymer network Commun. Chem. 2 97

[33] Lee W H and Park Y D 2017 Tuning electrical properties of 2D materials by self-assembled monolayers Adv. Mater. 1700316

[34] You P, Tang G and Yan F 2019 Two-dimensional materials in perovskite solar cells Mater. Today Energy 11 128–58

[35] Muratov D S et al 2019 Slot-Die printed two-dimensional ZrS3 charge transport layer for perovskite light-emitting diodes ACS Appl. Mater. Interfaces Interfaces 11 48021–8

[36] Konios D, Kakavelakis G, Petridis C, Savva K, Stratakis E and Kymakis E 2016 Highly efficient organic photovoltaic devices utilizing work-function tuned graphene oxide derivatives as the anode and cathode charge extraction layers J. Mater. Chem. A 4 1612–23

[37] Najiﬁ L et al 2018 MoS2 quantum dot/graphene hybrids for advanced interface engineering of a CHNH3PbI3 perovskite solar cell with an efﬁciency of over 20% ACS Nano 12 10736–54

[38] Xu X, Liu C, Sun Z, Cao T, Zhang Z, Wang E, Liu Z and Liu K 2018 Interfacial engineering in graphene bandgap Chem. Soc. Rev. 47 3059–74

[39] Volonakis G and Giustino F 2015 Ferroelectric graphene-perovskite interfaces J. Phys. Chem. Lett. 6 2496–302

[40] Volonakis G and Giustino F 2018 Interfaces between graphene-related materials and MAPbI3: insights from first-principles Adv. Mater. Interfaces 5 1800496

[41] Wang W-W, Tang J-S, Jia R, Segawa H and Sugimoto M 2018 A first-principles prediction on ‘healing effect’ of graphene preventing carrier trapping near the surface of metal halide perovskites Chem. Sci. 9 3341–53

[42] Agresti A, Pescettelli S, Taheri B, Del Rio Castillo A E, Cinà L, Bonaccorso F and Di Carlo A 2016 Graphene-perovskite solar cells exceed 18% efﬁciency: a stability study Chem. Sus. Chem. 9 2609–19

[43] Busby Y, Agresti A, Pescettelli S, Di Carlo A, Noel C, Pireaux J-J and Houssiau L 2018 Aging effects in interface-engineered perovskite solar cells with 2D nanomaterials: a depth proﬁle analysis Mater. Today Energy 9 1–10

[44] O’Keeffe P et al 2019 Graphene-induced improvements of perovskite solar cell stability: effects on hot-carriers Nano Lett. 19 684–91

[45] Agresti A et al 2017 Graphene interface engineering for perovskite solar module: 12.6% power conversion efﬁciency over 50 cm2 active area ACS Energy Lett. 2 279–87

[46] Das S, Pandey D, Thomas J and Roy T 2019 The role of graphene and other 2D materials in photovoltaics Adv. Mater. 31 1–35

[47] Khazaei M, Arai M, Sasaki T, Ranjbar A, Liang Y and Yunoki S 2015 OH-terminated two-dimensional transition metal carbides and nitrides as ultralow work function materials Phys. Rev. B: Condens. Matter Mater. Phys. 92 1–10

[48] Hu T, Li Z, Hu M, Wang J, Hu Q, Li Q and Wang X 2017 Chemical origin of termination-functionalized MXenes: Ti3C2T2 as a case study J. Phys. Chem. C 121 19254–61

[49] Liu Y, Xiao H and Goddard W A 2016 Schottky-barrier-free contacts with two-dimensional semiconductors by surface-engineered MXenes J. Am. Chem. Soc. 138 15853–6

[50] Guo Z, Gao L, Xu Z, Teo S, Zhang C, Kamata Y, Hayase S and Ma T 2018 High electrical conductivity 2D MXene serves as additive of perovskite for efﬁcient solar cells Small 14 1802738

[51] Yang L et al 2019 SnO2–Ti3C2 MXene electron transport layers for perovskite solar cells J. Mater. Chem. A 7 5635–42

[52] Agresti A et al 2019 Titanium-carbide MXenes for work function and interface engineering in perovskite solar cells Nat. Mater. 18 1228–34

[53] Ameen S, Akhtar M S, Seo H, Nazeeruddin M K and Shin H 2015 An insight into atmospheric plasma jet modi Fi Ed ZnO quantum dots thin ﬁlm for ﬂexible perovskite solar cell: optoelectronic transient and charge trapping studies J. Phys. Chem. C 119 10379–90

[54] Xiaojuan Z et al 2018 Efﬁcient planar perovskite solar cells with improved ﬁlter factor via interface engineering with graphene Nano Lett. 18 2442–9

[55] Huang P, Yuan L, Zhang K, Chen Q, Zhou Y, Song B and Li Y 2018 Room temperature and aqueous solution-processed 2D TiS2 as electron transport layer for highly efﬁcient and stable planar n-i-p Perovskite solar cells ACS Appl. Mater. Interfaces Interfaces 22 14796–802

[56] Yang L, Dall’Agnese C, Dall’Agnese Y, Chen G, Gao Y, Sanehira Y, Jena A K, Wang X-F, Gogotsi Y and Miyasaka T 2019 Surface-modified metallic Ti3C2T2 MXene as electron transport layer for planar heterojunction perovskite solar cells Adv. Funct. Mater. 29 1905694

[57] Zhao X et al 2019 20% Efﬁcient perovskite solar cells in planar transport layer Adv. Funct. Mater. 29 1805168

[58] Ruy J, Lee J W, Yu H, Yun J, Lee K, Lee J, Hwang D, Kang J, Kim S K and Jang J 2017 Size effects of graphene quantum dots modiﬁed-blocking TiO2 layer for efﬁcient planar perovskite solar cells JaeHoon J. Mater. Chem. A 5 16834–42

[59] Cho K T, Grancini G, Lee Y, Konios D, Paek S, Kymakis E and Nazeeruddin M K 2016 Beneﬁcial role of reduced graphene oxide for electron extraction in highly efﬁcient perovskite solar cells Chem. Sus. Chem. 9 3040–4

[60] Mahmoudi T, Wang Y and Hahn Y 2019 SrTiO3/Al2O3-graphene electron transport layer for highly efﬁcient and stable perovskite-based perovskite solar cells with 20.6 % efﬁciency Adv. Electron. Mater. 10 1903569

[61] Mals S, Shint H, Kima H and Hong C K 2016 Reduced graphene oxide (RGO) grafted zinc stannate (Zn2SnO4) nanofibers scaffolds for highly efﬁcient mixed-halide perovskite solar cells J. Mater. Chem. A 4 12158–69

[62] Agresti A et al 2017 Graphene interface engineering for perovskite solar cells 12.6% power conversion efﬁciency over 50 cm2 active area ACS Energy Lett. 2 279–87

[63] Wang Y, Wang S, Chen X, Li Z, Wang J, Li T and Deng X 2018 Large-scale enhanced VOC and stability in perovskite solar cells with modiﬁed energy match by couple 2D interlayers J. Mater. Chem. A 6 4860–7

[64] Huang P, Chen Q, Zhang K, Yuan L, Zhou Y, Song B and Li Y 2019 21.7% Efﬁciency achieved in planar n-i-p perovskite solar cells via interface engineering with water-soluble 2D TiS2 Peng J. Mater. Chem. A 7 6215–9
[65] Dong H et al 2019 Conjugated molecules ‘bridge’: functional ligand toward highly efficient and long-term stable perovskite solar cell Adv. Funct. Mater. 29 1808119

[66] Fang X, Ding J, Yuan N, Sun P, Lv M, Ding G and Zhu C 2017 Graphene quantum dot incorporated perovskite films: passivating grain boundaries and facilitating electron extraction Phys. Chem. Chem. Phys. 19 6057–63

[67] Hadadian M et al 2016 Enhancing efficiency of perovskite solar cells via N-doped graphene: crystal modification and surface passivation Adv. Mater. 28 8681–6

[68] Chung C, Narra S, Jokar E, Wu H and Wei-guang E 2017 Inverted planar solar cells based on perovskite/graphene oxide hybrid composites J. Mater. Chem. A: Mater. Energy Sustain. 5 13957–63

[69] Wang Y, Zhang H, Zhang T, Shi W, Kan M, Chen J and Zhao Y 2019 Photostability of MAPbI$_3$ perovskite solar cells by incorporating black phosphorus Sol. RRL 3 1900197

[70] Zhou T, Lai H, Liu T, Lu D, Wan X, Zhang X, Liu Y and Chen Y 2019 Highly efficient and stable solar cells based on crystalline oriented 2D/3D hybrid perovskite Adv. Mater. 31 1901242

[71] Tang G et al 2019 Solution-phase epitaxial growth of perovskite films on 2D material flakes for high-performance solar cells Adv. Mater. 31 1807689

[72] Zhang F, He J, Xiang Y, Zheng K, Xue B, Ye S and Peng X 2018 Semimetal – semiconductor transitions for monolayer antimonene nanosheets and their application in perovskite solar cells Adv. Mater. 30 1803244

[73] Jung E H, Jeon N J, Park E Y, Moon C S, Shin T J, Yang T Y, Noh J H and Seo J 2019 Efficient, stable and scalable perovskite solar cells using poly(3-Hexylthiophene) Nature 567 311–5

[74] Chen H et al 2016 Extending the environmental lifetime of unpackaged perovskite solar cells through interfacial design J. Mater. Chem. A 4 11604–10

[75] Yang Q-D, Cheng Y, Li H-W, Guan Z, Yu B, Li J and Tsang S-W 2017 Graphene oxide as efficient hole transporting material for high-performance perovskite solar cells with enhanced stability J. Mater. Chem. A 5 9852–8

[76] Huang P, Wang Z, Liu Y, Zhang K, Yuan L, Zhou Y, Song B and Li Y 2017 Water-soluble 2D transition metal dichalcogenides as hole transport layer for high efficient and stable p-i-n perovskite solar cells ACS Appl. Mater. Interfaces 9 25323–31

[77] Moduk K S, Varsha A, Arvind S, Han G, Thirumal K, Lev O, Mhaisalkar S and Mathews N 2017 2D black phosphorous nanosheets as a hole transporting material in perovskite solar cells J. Power Sources 371 156–61

[78] Chu Q et al 2019 Highly stable carbon-based perovskite solar cell with a record efficiency of over 18 % via hole transport engineering J. Mater. Sci. Technol. 35 987–93

[79] Luo Q, Zhang Y, Liu C, Li J, Wang N and Lin H 2015 Iodide-reduced graphene oxide with dopant-free spiro-OMeTAD for ambient stable and high-efficiency perovskite solar cells J. Mater. Chem. A 3 15996–6004

[80] Dai R, Wang Y, Yang J and Deng X 2017 Metal-organic compound branched MoS$_2$ for achieving high performance perovskite solar cells Chem. Sus. Chem. 10 2869–74

[81] Li D, Cai J, Li H, Huang D, Wang M and Shen Y 2016 Science direct graphene oxide modified hole transport layer for CH$_3$(NH$_2$)PbI$_3$ planar heterojunction solar cells Sol. Energy 131 176–82

[82] Chen T, Tong G, Xu E, Li H, Li P, Zhu Z, Tang J, Li Y and Jiang Y 2019 Accelerating hole extraction by inserting 2D Ti$_2$C$_2$-MXene interlayer to all inorganic perovskite solar cells with long-term stability J. Mater. Chem. A 7 20597–603

[83] Sung H, Ahn N, Jang M S, Lee J, Yoon H, Park N and Choi M 2016 Transparent conductive oxide-free graphene-based perovskite solar cells with over 17 % efficiency Adv. Energy Mater. 6 1501873

[84] Lu H, Sun J, Zhang H, Lu S and Choy W C H 2016 Room-temperature solution-processed and metal-oxide-free nano-composite for the flexible transparent bottom electrode of perovskite solar cells Nanoscale 8 5946–53

[85] Lang F et al 2015 Perovskite solar cells with large-area CVD-graphene for tandem solar cells perovskite solar cells with large-area CVD-graphene for tandem solar cells J. Phys. Chem. Lett. 6 2745–50

[86] Lamanna E et al 2020 Mechanically stacked, two-terminal graphene-based perovskite/silicon tandem solar cell with efficiency over 26% Joule 4 1–17

[87] Fan Z et al 2017 Layer-by-layer degradation of methylammonium lead tri-iodide perovskite microplates layer-by-layer degradation of methylammonium lead tri-iodide perovskite microplates Joule 15 1–15

[88] Yu H et al 2018 Waterproof perovskite-hexagonal boron nitride hybrid nanolasers with low lasing thresholds and high operating temperature waterproof perovskite-hexagonal boron nitride hybrid nanolasers with low lasing thresholds and high operating ACS Photonics 5 4920–8

[89] Zhao L, Tian H, Scott H, Kahn A and Rand B P 2018 Ultrasmall heterojunctions of graphene and 2D perovskites reveal spontaneous iodide loss ultrasmall heterojunctions of graphene and 2D perovskites reveal spontaneous iodide loss Joule 2 2133–44

[90] Arora N, Dar M I, Hinderhofer A, Pellet N, Schreiber F, Zakeeruddin S M and Gritzel M 2017 Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20% Science 355 768–71

[91] Kakavelakis G et al 2018 Extending the continuous operating lifetime of perovskite solar cells with a molybdenum disulfide hole extraction layer Adv. Energy Mater. 8 1702287

[92] Tsirkrizis O et al 2020 A two-fold engineering approach based on Bi$_2$T$_3$ flakes towards efficient and stable inverted perovskite solar cells Mater. Adv. 1 450–62

[93] Zheng Y, Niu T, Ran X, Qiu J and Li B 2019 Unique characteristics of 2D Ruddlesden–Popper (2DPP) perovskite for future photovoltaic application J. Mater. Chem. A: Mater. Energy Sustain. 7 13860–72

[94] Guo W, Shi J, Zhu Y, Wu M, Du J, Cen Y, Liu S and Han S 2020 Two-dimensional 111-type in-based halide perovskite Cs$_2$I$_3$ In$_2$X$_3$ (X = Cl, I) with optimal band gap for photovoltaics and defect-insensitive blue emission Phys. Rev. Appl. 13 024031

[95] Pan L, Ding Y, Yu Z, Wan Q, Liu B and Cai M 2020 Layer-dependent optoelectronic property for all-inorganic two-dimensional mixed halide perovskite Cs$_2$PbI$_3$Cl$_2$ with a Ruddlesden-Popper structure J. Power Sources 451 227732

[96] Wei Y, Feng G, Mao P, Luan Y and Zhuang J 2020 Lateral photodetectors based on double-cable polymer/2D perovskite heterojunction ACS Appl. Mater. Interfaces 12 8826–34

[97] Zhao Y, Ma Q, Liu B, Yu Z, Yang J and Cai M 2018 Layer-dependent transport and optoelectronic property in two-dimensional perovskite: (PEA)$_2$PbI$_4$ Nanoscale 10 8677–88

[98] Ding Y, Zhao Q, Yu Z, Zhao Y, Liu B, He F, Zhou H, Li K, Yin S and Cai M 2019 Strong thickness-dependent quantum confinement in all-inorganic perovskite Cs$_2$PbI$_4$ with a Ruddlesden-Popper structure J. Mater. Chem. C 7 7433–41

[99] Dou L 2017 Emerging two-dimensional halide perovskite nanomaterials J. Mater. Chem. C 5 11165–73

[100] Blancan J C et al 2017 Extremely efficient internal exciton dissociation through edge states in layered 2D perovskites Science 355 1288–92
[101] Thrithamarassery Gangadharan D and Ma D 2019 Searching for stability at lower dimensions: current trends and future prospects of layered perovskite solar cells Energy Environ. Sci. 12 2860–89
[102] Yang R et al 2018 Oriented Quasi-2D perovskites for high performance optoelectronic devices Adv. Mater. 30 1804771
[103] Kim D et al 2020 Efficient, stable silicon tandem cells enabled by anion-engineered wide-bandgap perovskites Science 368 155–60
[104] Grancini G et al 2017 One-year stable perovskite solar cells by 2D/3D interface engineering Nat. Commun. 8 1–8
[105] Agresti A, Pescetelli S, Palma A L, Martin-Garcia B, Najafi L, Bellani S, Moreh I, Prato M, Bonaccorso F and Di Carlo A 2019 Two-dimensional (2D) material interface engineering for efficient perovskite large-area modules ACS Energy Lett. 4 1862–71
[106] Pescetelli S, Castriotta L A, Agresti A and Di Carlo A 2019 Large area perovskite solar modules with improved efficiency and stability 2019 Int. Symp. Adv. Electr. Commun. Technol. pp 1–5
[107] Jariwala D, Davoyan A R, Wong J and Atwater H A 2017 Van Der Waals materials for atomically-thin photovoltaics: promise and outlook Van Der Waals materials for atomically-thin photovoltaics: promise and outlook ACS Photonics 4 2962–70