An improvement in un-Encapsulated perovskite solar cell’s environmental stability via introduction of an electrode interface layer

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\textbf{ABSTRACT}

Perovskite solar cells (PSCs) have shown power conversion efficiency (PCE) up to 25.5%, but they are still struggling with their poor environmental stability. We have improved the ecological stability of un-encapsulated PSCs via interface modification of the top metal electrode. We used CH$_3$NH$_3$PbI$_3-x$Cl$_x$ perovskite as the light absorber and Ag metal as the top electrode. The interface of Ag electrode was modified by introducing a thin layer of MoO$_x$/Al before Ag. We observed that MoO$_x$/Al interlayer before Ag imparts better stability to the devices than conventional Ag electrode only. We found that MoO$_x$/Al interlayer impedes the diffusion of oxygen and metal electrode into the perovskite film and considerably halts the device degradation upon being kept for about 350 h under laboratory ambient conditions (room temperature 25±2°C and humidity 40±5%). This work mainly highlights the role of interfaces in PSCs degradation, and will help to address the stability issues in PSCs.
Introduction

Perovskite semiconductors have shown excellent electrical and optical properties [1–3], which make them suitable for a variety of applications in solar cells [4], light-emitting diodes [5], detectors [6], etc. Perovskite solar cells (PSCs) have shown an enormous possibility for the cost-effective conversion of solar energy into electrical energy. The first PSC was fabricated in 2009, which had an efficiency of ~ 3.8%, and since then, there has been a remarkable improvement in its performance. Now, the efficiency has gone beyond 25% [1], approaching that of the conventional Si solar cells [7,8]. The materials and the processing cost of PSCs are very low compared to other solar cell technologies [9]. But the long-term stability is a critical issue, and these devices degrade very fast in ambient conditions; for the successful commercialisation of PSCs, the issue of poor stability needs to be sorted out. PSCs are thin film solar cells, and the thin films of perovskite semiconductors are mainly prepared by spin coating technique; for scalable large area fabrication, other coating techniques like spray coating [10], doctor bladed coating [11], slot die coating [12], screen printing [13] and thermal deposition [14,15] are also well established. PSCs incorporate multiple thin layers of different materials playing different roles in the solar cells, such as light-absorbing perovskite layer (active layer) like methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$), methylammonium lead iodide chloride (CH$_3$NH$_3$PbI$_{3-n}$Cl$_n$), formamidinium lead iodide (CH$_{(3-n)}$(NH$_2$)$_n$PbI$_3$) etc., electron transport layer (ETL) like titanium oxide (TiO$_2$) [16], tin oxide (SnO$_2$) [17,18], phenyl C$_{61}$ butyric acid methyl ester (PCBM) [19] etc. and hole transport layer (HTL) like poly(3-hexylthiophene) (P3HT) [20], 2,2’,7,7’-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene (Spiro-MeOTAD) [21], nickel oxide (NiO$_x$) [22] etc. along with top and bottom electrodes. One of the electrodes is optically transparent, and for that purpose, transparent conducting oxides (TCOs) such as fluorine-doped tin oxide (FTO) and indium tin oxide (ITO) are used, whereas for other electrode metals like Al, Ag, Au, Cu, etc. are used.

The performance of PSCs depends upon the material purities, processing methods, and environmental growth conditions. Small variations in these parameters lead to a significant change in the performance of PSCs [23]. The ageing of the perovskite precursor is also an important parameter that needs to be considered for maximum solar cell performance. Su et al. investigated the effect of perovskite precursor ageing on the PSCs performance and found that an ageing time of 6 h was optimal for maximum performance of the solar cells [24]. The solar cells fabricated with freshly made precursor solution and excessively aged precursor solution resulted in the formation of inferior perovskite films with poor absorption and increased recombination sites. The solar cells prepared with 6 h aged precursor solution led to the formation of solar cells with greater efficiency, stability, and reproducibility. In addition to these factors, the defects and the non-radiative losses in the perovskite layers have also been observed to result in inferior device performance. Therefore, efforts are also being made to passivate the defects in perovskite films. Cai et al. used potassium oleate (KOA) as an interface modifier at the perovskite-HTL interface and achieved over 23% efficiency and quite a high open-circuit voltage ($V_{oc}$) of 1.16 V [25]. It was observed that KOA plays a multi-functional role, where K$^+$ ions penetrate the perovskite layer and fill the $+$ve charge vacancy, and the COO$^{-}$ group coordinates with Pb$^{2+}$ ions and passivates the defects, the hydrophobic long-chain olefins cover the perovskite and imparts environmental stability to the devices. PSCs exhibit degradation and show considerable loss of photovoltaic efficiency when exposed to oxygen, moisture, UV light, and high temperature [26–30]. The degradation dominantly occurs within the light-absorbing active layer [31]. Still, it is greatly affected by the performance and thicknesses of the HTL, ETL, and the electrode materials used in solar cells [32]. Degradation occurs because of chemical reactions taking place in solar cells, and the chemical reactions occur not only between the interlayers, such as the perovskite layer, and the ETL or HTL, but the chemical reactions also take place when the metal electrode diffuses into the perovskite layer and reacts there to cause degradation in device performance [29–35]. However, adding the metal oxide buffer layers between the perovskite layer and the metal electrode has been observed to reduce the direct diffusion of the metal electrode into the perovskite layers [35, 36,37].

We have investigated and reported here the environmental stability of the PSCs via adding a metal oxide buffer layer such as MoO$_x$ between the HTL and the metal electrode. Usually, Ag is used as an anode in conjunction with HTL for hole extraction, but Ag has shown to react rapidly with the perovskite layer [29]. Because of the Ag reaction with the perovskite layer, both Ag electrode and perovskite light absorber lose their electrical properties, and solar cell efficiency decays very rapidly. Here, in addition to MoO$_x$, we have also used a thin layer of Al before Ag to impede the diffusion of both the oxygen and Ag into the perovskite layer. The performance of un-encapsulated solar cells with Ag and MoO$_x$/Al/Ag electrodes was studied from time to time for degradation in their efficiency. We have observed that the devices with
MoO₃/Al/Ag electrode were more stable than the conventional devices with Ag electrodes only.

**Experimental details**

**Materials**

For the fabrication of PSCs, we have used FTO-coated glass substrates (sheet resistance ~7 Ω/sq), 15% tin oxide (SnO₂) colloidal dispersion in H₂O, methylammonium iodide (MAI) (CH₃NH₃I), lead iodide (PbI₂), lead chloride (PbCl₂), 2,2’,7,7’-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene (Spiro-MeOTAD), 4-tert-butylpyridine (TBP), bis(trifluoromethane) sulfonamide lithium salt (LiTFSI), anhydrous dimethylformamide (DMF), anhydrous chloroform, anhydrous acetonitrile, Ag metal (99.999%), Al metal (99.999%), and molybdenum oxide (MoO₃). All the materials like FTO substrate, MAI, PbI₂, PbCl₂, Spiro-MeOTAD, TBP, LiTFSI, MoO₃, anhydrous chloroform, acetonitrile, DMF, Ag, and Al were purchased from Aldrich Chemicals, USA, whereas SnO₂ colloidal solution was purchased from Alfa Aesar, USA. All the materials were used as received from their respective sources.

**Growth and characterisation of perovskite films**

For the solar cell fabrication, we used FTO-coated glass substrates and deposited a thin layer of SnO₂ before perovskite film, which serves as the compact hole blocking and ETL in the solar cells [38]. The growth of the perovskite layer depends very strongly on the surface energy of the underlying layer/film and the substrate [39]. To avoid any possible morphological changes and disparity in other properties of the perovskite films due to variation in the surface energy of the underlying substrate, for individual film characterisation, all the perovskite films were grown on SnO₂ coated FTO substrates only. This assured that the properties of the perovskite active layer in the solar cells were the same as studied here. Proceeding to any deposition, the FTO substrates were cleaned sequentially with soap solution, distilled water, acetone, and isopropyl alcohol, and treated with air plasma for 20 minutes in a plasma chamber. After that, 15% colloidal dispersion of SnO₂ in water was spin-coated on the FTO substrates at 2000 rpm for 60 sec. and annealed at 120°C for 60 min. in the air to form a compact SnO₂ film. After the samples were cooled down to room temperature, they were subjected to air plasma treatment for 5 min. The air plasma treatment increases the surface energy and reduces the contact angle of SnO₂. For the contact angle measurement, a drop of distilled water was put on the SnO₂ film before and after the plasma treatment, and the contact angles were measured. The contact angle of the SnO₂ film without plasma treatment was measured to be ~43°, and after the air plasma treatment, the contact angle was reduced to ~4°. The photographs of the contact angle measurements of both cases are shown in Fig. S1 of the supplementary information. Further, for the growth of the perovskite films, the samples with plasma-treated SnO₂ film were transferred to a glove box filled with high purity dry nitrogen (O₂ < 1 ppm, H₂O < 1 ppm). The perovskite precursor was prepared by mixing MAI, PbI₂, and PbCl₂ in 4:1:1 molar ratio in anhydrous DMF and spin-coated over SnO₂ coated FTO substrates at 3000 rpm for 60 sec. and annealed at 100°C for 60 min. This resulted in the conversion of pale yellow film into dark brown film, which indicated the formation of CH₃NH₃PbI₃·Clₓ perovskite crystals. The fabrication of perovskite films is schematically shown in Figure 1. Further, these samples were used for the essential characterisation like light absorption, crystal structure, and surface morphology of the perovskite films. For light absorption, crystal structure, and surface morphology, the

![Figure 1. Schematic representation of the growth of perovskite film on a glass substrate by spin coating method.](image-url)
Perovskite solar cells fabrication

PSCs were prepared on $2 \times 2$ cm$^2$ FTO-coated glass substrates, and the substrates were patterned to remove unwanted FTO from the substrate for device fabrication. Prior to any deposition, the patterned substrates were cleaned and air plasma treated for 15 min. The schematic structure of the PSCs with Ag electrode only is shown in Figure 2(a), whereas Figure 2(b) shows the photograph of the solar cell. Here FTO works as the cathode, and Ag works as the anode. We used SnO$_2$ as an electron transport layer (ETL) because SnO$_2$ is an oxygen-deficient n-type semiconductor and the light absorbing layer was a mixed halide perovskite film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. The patterned FTO substrates were coated with SnO$_2$ first and then with CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite on the SnO$_2$ layer. The methods of growth of both layers are discussed in the previous section. For the HTL, we used Spiro-MeOTAD as a p-type organic semiconductor. Spiro-MeOTAD films were prepared by spin coating of its 75 mg/ml solution in anhydrous chloroform, doped with 28 µl of TBP and 17.5 µl of 520 mg/ml solution of LiTFSI in acetonitrile, at 2000 rpm for 60 sec. To complete the solar cells, 100 nm of Ag was thermally deposited at 1 Å/s onto Spiro-MeOTAD through a shadow mask in a vacuum chamber at the base pressure of $2 \times 10^{-6}$ mbar, which resulted in the device active area of $\sim 0.09$ cm$^2$.

For the PSCs with modified structure with MoO$_x$/Al interlayer in between the Spiro-MeOTAD and Ag electrode, all the fabrication steps up to Spiro-MeOTAD HTL were identical as both type of devices were prepared together. It is worth mentioning here that in most efficient PSCs, the HTL is usually a thin layer of Spiro-MeOTAD doped with tert-butylpyridine (TBP) and Lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) [22]. However, the hygroscopic nature of Li-TFSI leads to rapid degradation in cell performance in a moist environment. For a more robust and stable HTL, we deposited a thin layer of MoO$_x$ for protection from environmental degradation. 20 nm of MoO$_x$ was thermally deposited on Spiro-MeOTAD in a vacuum chamber at 0.5 Å/s, at the base pressure of $2 \times 10^{-6}$ mbar. Then, quite a thin layer of 30 nm of Al was deposited by thermal evaporation through a shadow mask, followed by thermal deposition of 80 nm of Ag at 1 Å/s through the same mask, at the base pressure of

Figure 2. (a) Schematic structure of the PSC with Ag only as the top electrode. (b) Photograph of one of the PSCs.
The structure of the modified devices is shown schematically in Figure 3. As a whole, two types of solar cells were prepared FTO/SnO$_2$/Perovskite/Spri-MeOTAD/Ag and FTO/SnO$_2$/Perovskite/Spri-MeOTAD/MoO$_3$/Al/Ag and studied for their air stability.

Solar cell characterisation

HT To determine the photovoltaic parameters and the PCE of PSCs, the solar cells were exposed to 100 mW/cm$^2$ illumination of an AM1.5 G class AAA solar simulator from Photo Emission Tech (PET), USA, and tested for their current density-voltage ($I-V$) characteristics under illumination using a Keithley 2420 SourceMeter unit (SMU) interfaced with a computer. The photovoltaic parameters were extracted from the illuminated $I-V$ characteristics that led us to calculate the PCE. To obtain the degradation profiles of solar cells, they were stored and tested in ambient air for their PCE at regular time intervals. The solar cells were not encapsulated or protected externally by any means for these studies.

Results and discussion

Figure 4 shows the XRD patterns of the FTO substrate and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ film deposited on the SnO$_2$-coated FTO glass substrate. In the XRD pattern of the FTO/SnO$_2$/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ sample, the diffraction peaks occurred at 20 values of 14.2°, 28.6°, 43.2°, and 58.8°, which corresponded to the (110), (220), (330) and (440) planes of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite and it indicated the formation of highly crystalline tetragonal phase of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite [40–44]. The intensity of XRD peaks corresponding to (110) and (220) planes of the perovskite was very much dominating compared to the peaks at (330) and (440), which indicates that the growth of the perovskite crystals was oriented towards (110) and (220) planes. The XRD peaks of FTO and SnO$_2$ were not visible in the XRD pattern of the FTO/SnO$_2$/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ sample because the intensity of XRD peaks of perovskite film was so dominating that the XRD peaks for FTO and SnO$_2$ were not visible. Figure 5 shows the UV-vis absorption spectrum of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite film on the FTO/SnO$_2$ substrate. Since SnO$_2$ film was quite thin (∼40 nm) and it is a wide band gap material (3.8 eV), the absorption contribution of SnO$_2$ in the absorption graph was not visible. The absorption graph shown in Figure 5 corresponds to absorption in the perovskite film only. The perovskite film exhibited broad light absorption spanning from 300 to 850 nm. From the extrapolation of the linear part of the absorption spectrum at the absorption edge to zero absorption and using the Tauc’s relationship, the perovskite film’s bandgap was found to be 1.55 eV. Figure 6 shows the FE-SEM image of the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite film on the FTO/SnO$_2$ substrate. The perovskite film was quite good; we did not see any holes or irregularities in the film, and it covered the substrate completely. The size of perovskite grains was quite large, up to a few microns. Large grain size results in reduced recombination of photo-generated charge carriers and, as a result, higher PCEs.

Figure 7 shows the $J-V$ characteristics of the champion PSC with Ag electrode only. The photovoltaic parameters of the champion cell are given in the inset of the figure. The solar cell exhibited a short circuit current density ($J_{sc}$) of 20.8 mA/cm$^2$, open-circuit voltage ($V_{oc}$) of 0.85 V, fill factor (FF) of 0.68, and PCE of 12%. The average PCE of the three devices with Ag electrodes was only 11.5 ± 0.5%. The $J-V$ characteristics of the champion cell with MoO$_3$/Al interlayer are shown in Figure 8, and the photovoltaic
parameters are shown in the inset of the figure. The champion solar cell with MoO_x/Al interlayer exhibited J_{sc} of 20.4 mA/cm^2, V_{oc} of 0.84 V, FF of 0.60, and PCE of 10.3%. The average PCE of the three devices with MoO_x /Al interlayer and Ag electrode was 9.7 ± 0.6%. The reason behind the marginal decrease in the PCE with MoO_x/Al interlayer electrode was that adding buffer layer MoO_x possibly introduces some series resistance for charge extraction and enhances the charge recombination at the interface between the perovskite and the MoO_x layer, or MoO_x acts like an energy barrier limiting its hole extraction efficiency [45]. Direct deposition of Ag metal electrode on the MoO_x layer leads to the lowering of the device’s PCE [45]. Moreover, when Al is deposited on the MoO_x layer, the perovskite solar cells show a marginal decrease in PCE; however, further deposition of Ag metal electrode on the top of the MoO_x/Al layer renders the perovskite solar cells environmentally stable. The top layer combination of MoO_x/Al/Ag prevented the further diffusion of oxygen and moisture into the PSCs’ active layer, hence stable PCE.

Both types of devices were stored together in air with the temperature being 25 ± 2°C and relative humidity being 40 ± 5% without encapsulation and tested for degradation in their PCE from time to time. Figure 9(a) shows the photographs of both solar cells taken at zero hours and after 200 h. It is evident from the photographs that in PSCs with Ag electrode only, the active area of solar cells gets completely decomposed into lead iodide showing yellow colour within 200 h but using a combination of MoO_x/Al before Ag electrode, the PSCs active area remained safe from the effect of oxygen and moisture diffusion. The solar cells’ normalised PCE profiles as a function of time are shown in Figure 9.
The profile of PSCs with Ag electrode only suggests the occurrence of rapid degradation due to which the PCE decreased from 12% to less than 1% within 150 h; however, no such rapid degradation was found to happen with MoO$_x$/Al interlayer before Ag, as it retained up to 90% of the initial PCE for up to 350 h, i.e. marginal degradation in PCE from an initial value of 10.3% to 9.3% after 350 h was observed. This can be attributed to the fact that the MoO$_x$ layer prevents further diffusion of the metal electrode into the active layer, and the combination of Al made solar cells more environmentally stable. The role of the MoO$_x$/Al interface layer can be better understood from the model shown in Figure 10. A thin layer of MoO$_x$ along with Al provides greater resistance to the oxygen and moisture diffusion into the device. Here, the degradation of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ happens exactly in the same way as that of CH$_3$NH$_3$PbI$_3$ in air. The oxygen and moisture diffusion into the devices without the MoO$_x$ layer leads to the decomposition of perovskite into CH$_3$NH$_3$I, PbI$_2$, and PbCl$_2$. CH$_3$NH$_3$I decomposes to CH$_3$NH$_2$ and HI. HI releases I$_2$ in the presence of oxygen. The I$_2$ releases through HTL and reacts with the Ag electrode to form AgI [46]. The remaining product left in the perovskite film is PbI$_2$, which is yellow. The chemical reactions in the PSCs are shown in Fig. S2 of the supplementary information, which is in accordance with other reports [47–49]. The chemical reactions in the solar cells result in severe losses in their optical and electrical properties. Qi et al. reported that when perovskite solar cells were exposed to the air, Spiro-MeOTAD enhanced the
Figure 9. (a) Photographs of solar cells with and without MoOx/Al interface layer at zero hours and after 200 h in air. (b) Degradation profiles of the normalised PCE of FTO/SnO2/Perovskite/Spiro-MeOTAD/Ag and FTO/SnO2/Perovskite/Spiro-MeOTAD/MoOx/Al/Ag solar cells as a function of time.

Figure 10. (a) Schematic representation of diffusion of oxygen and moisture into the PSCs without MoOx/Al interface layer before Ag electrode and (b) schematic representation of prevention of diffusion of oxygen and moisture into the PSCs with MoOx/Al interface layer.
degradation in the conventional perovskite solar cells structure [50], with Li-TFSI migrating from the bottom to the top across the Spiro-MeOTAD film. Here, Li-TFSI slowly accumulated at the top surface of HTL and induced rapid film degradation. However, the introduction of the MoOx layer at the top of the Spiro-MeOTAD film forms an oxide layer (upon the reaction of MoOx with oxygen), which acts as an oxygen barrier and prevents the further diffusion of oxygen into the perovskite layer and thus, the stability of the device is retained. These results suggest that the MoOx/Ag interlayer along with the Ag electrode imparts better stability to PSCs than the conventional solar cells structure with an Ag electrode only. Here, the MoOx and Al/Ag electrode plays an important role in preventing the diffusion of oxygen and moisture into the active perovskite absorber layer and retaining the effective PCE. It is important to mention that here, a very thin layer of MoOx (~ 20 nm) may aid in pinning the work function at the spiro-OMeTAD interface with concurrent nucleation of a stable and passivating oxide layer, presumably Al2O3 at the (MoOx/Al) interface leading to higher stability of the device. A detailed investigation is underway to elucidate this mechanism.

Conclusions

The PSCs were prepared using a mixed halide CH3NH3PbI3-xClx perovskite as an active light absorber with SnO2 as ETL and Spiro-MeOTAD as HTL. The perovskite films were subsequently uniform and composed of large crystal grains. The PSCs with Ag electrodes degraded rapidly due to the diffusion of oxygen and moisture into the devices and their reaction with device constituents. The degradation of PSCs gets reduced with the introduction of the MoOx/Al interfacial layer before the Ag electrode. The introduction of the MoOx/Al interlayer decreases the diffusion of oxygen and moisture into the perovskite layer and prevents deterioration in the solar cell efficiency. Thus, the electrode interface layer plays a vital role in dictating the stability and efficiency of the PSCs. From the above perovskite device stability studies, it can be conjectured that both MoOx interlayer and MoOx/metal (Al, Ag) combination is imperative for the long-term stability of PSCs.

Disclosure statement

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References

[1] https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20200925.pdf.
[2] Green MA, Baille AH, Snaith HJ. The emergence of perovskite solar cells. Nat Photonics. 2014;8:506.
[3] Anbarasan R, Srinivasan M, Sundar JK, et al. Structural, electronic and optical properties of inorganic perovskite CsPb(1-x)GexI3: a first principle approach. Mater Technol. 2021. DOI:10.1080/10667857.2021.1915057
[4] Jung HS, Park NG. Perovskite solar cells: from materials to devices. Small. 2015;11:10.
[5] Li Y, Ma F, Zhao D, et al. Convenient synthesis of high-quality, all-inorganic lead halide perovskite nanocrystals for high purity monochrome QLED. Mater Technol. 2021;36(11):637.
[6] Sun L, Li W, Zhu W, et al. Single-Crystal perovskite detector: development and perspectives. J Mater Chem C. 2020;8:11664.
[7] Andreani LC, Bozolla A, Kowalczewski P, et al. Silicon solar cells: toward the efficiency limits. Adv Phys. 2019;4:1.
[8] Werner J, Barraud L, Walter A, et al. Efficient near-Infrared-Transparent perovskite solar cells enabling direct comparison of 4-Terminal and monolithic perovskite/silicon tandem cells. ACS Energy Lett. 2016;1:474.
[9] Rathore N, Panwar NL, Yettou F, et al. A comprehensive review of different types of solar photovoltaic cells and their applications. Internat J Ambi Energy. 2021;42(10):1200–1217.
[10] Bishop JE, Routledge TJ, Lidzey DG. Advances in spray-Cast perovskite solar cells. J Phys Chem Lett. 2018;9:1977.
[11] Deng Y, Dong Q, Bi C, et al. Air-stable, efficient mixed-cation perovskite solar cells with Cu electrode by scalable fabrication of active layer. Adv Energy Mater. 2016;6:1600372.
[12] Whitaker JB, Kim DH, Larson BW, et al. Scalable slot-die coating of high performance perovskite solar cells. Sustain Energy Fuels. 2018;2:2442.
[13] Rong Y, Ming Y, Ji W, et al. Toward industrial-scale production of perovskite solar cells: screen printing, slot-Die Coating, and emerging techniques. J Phys Chem Lett. 2018;9:2707.
[14] Li J, Wang H, Chin XY, et al. Highly efficient thermally co-evaporated perovskite solar cells and mini-modules. Joule. 2020;4(5):1035–1053.
[15] Hossain MI, Zakaria Y, Zikri A, et al. E-beam evaporated hydrophobic metal oxide thin films as carrier transport materials for large scale perovskite solar cells. Mater Technol. 2022;37(4):248–259.
[16] Yun JH, Lyu M, Ahmed R, et al. Desirable TiO2 compact films for nanostructured hybrid solar cells. Mater Technol. 2020;35(1):31–38.
[17] Park SY, Zhu K. Advances in SnO2 for efficient and stable n-i-p perovskite solar cells. Adv Mater. 2022;34:2110438.
[18] Alla M, Bimili S, Manjunath V, et al. Towards lead-free all-inorganic perovskite solar cell with theoretical efficiency approaching 23%. Mater Technol. 2022. DOI:10.1080/10667857.2022.2091195
[19] Ke QB, Wu JR, En Chiang S, et al. Improved performance of PCBM/MAPbI3 heterojunction photovoltaic cells with the treatment of a saturated BCP/IPA
solution. Sol. Energy Mater Sol Cells. 2022;242:111782.

[20] Jain S, Chaudhary N, Sharma SN. An insight into the mechanism of charge transfer of organic (P3HT): inorganic (CZTS) composites for hybrid photovoltaics. Mater Technol. 2022;37(8):684.

[21] Nakka L, Cheng Y, Aberle AG, et al. Analytical review of spiro-OMeTAD hole transport materials: paths toward stable and efficient perovskite solar cells. Adv Energy Sustain Res. 2022;3:2200045.

[22] Cui X, Jin J, Zou J, et al. NiOx nanocrystals with tunable size and energy levels for efficient and UV stable perovskite solar cells. Adv Funct Mater. 2022;32:2203049.

[23] Diao XF, Tang YL, Tang TYL, et al. Study on the stability of organic-inorganic perovskite solar cells materials based on first principle. Mole Physics. 2020;118(8):e1665200.

[24] Su J, Zheng X, Lang X, et al. Effect of precursor solution ageing time on the photovoltaic performance of perovskite solar cells. Funct Mater Lett. 2021;14:2151025.

[25] Cai F, Wu J, Pan W, et al. Potassium oleate as an effective interface modifier for defect passivation in planar perovskite solar cells. Funct Mater Lett. 2022;15:2251035.

[26] Kim JH, Williams ST, Cho N, et al. Enhanced environmental stability of planar heterojunction perovskite solar cells based on blade-Coating. Adv Energy Mater. 2015;5:1401229.

[27] Leijtens T, Eperon GE, Noel NK, et al. Stability of metal halide perovskite solar cells. Adv Energy Mater. 2015;5:1500963.

[28] Yang J, Siempelkamp BD, Liu D, et al. Investigation of CH3NH3PbI3 degradation rates and mechanisms in controlled humidity environments using in situ techniques. ACS Nano. 2015;9:1955.

[29] Chauhan AK, Kumar P. Degradation in perovskite solar cells stored under different environmental conditions. J Phys D Appl Phys. 2017;50:325105.

[30] Hany R, Lin H, Castro FA. Focus issue on organic and hybrid photovoltaics. Sci Tech Adv Mater. 2019;20(1):42.

[31] Hamed MSG, Mola GT. Mixed halide perovskite solar cells: progress and challenges. Critical Rev Sol Stat Mater Sci. 2020;45(2):85–112.

[32] Elangoan NK, Sivaprakasam A. Investigation of parameters affecting the performance of perovskite solar cells. Mol Cryst Liq Cryst. 2020;710(1):66.

[33] Chauhan AK, Kumar P, Pal SR, et al. Air-processed organo-metal halide perovskite solar cells and their air stability. J Mater Sci. 2017;52:10886.

[34] Sanehira EM, de Villers BJT, Schulz P, et al. Influence of electrode interfaces on the stability of perovskite solar cells: reduced degradation using MoOx/Al for hole collection. ACS Energy Lett. 2016;1:38.

[35] Jaffri SB, Ahmad KS. Interfacial engineering revolutionizers:perovskite nanocrystals and quantum dots accentuated performance enhancement in perovskite solar cells. Critical Rev Sol Stat Mater Sci. 2021;46(3):251.

[36] You J, Meng L, Song TB, et al. Improved air stability of perovskite cells via solution-processed metal oxide transport layers. Nat Nanotechnol. 2016;11:775.

[37] Zhao J, Zheng X, Deng Y, et al. Is Cu a stable electrode material in hybrid perovskite solar cells for a 30-year lifetime? Energy Environ Sci. 2016;9:3650.

[38] Kim MR, Kim SM, Bark CW. Characterization of perovskite solar cells with a solution processed two stage SnO2 electron transport layer. Mol Cryst Liq Cryst. 2021. DOI:10.1080/15421406.2021.1972230.

[39] Listorti A, Juarez-Perez EJ, Frontera C, et al. Effect of mesostructured layer upon crystalline properties and device performance on perovskite solar cells. J Phys Chem Lett. 2015;6(9):1628.

[40] Wang Q, Lyu M, Zhang M, et al. Transition from the tetragonal to cubic phase of organohalide perovskite: the role of chlorine in crystal formation of CH3NH3PbI3 on TiO2 substrates. J Phys Chem Lett. 2015;6(21):4379.

[41] Wang W, Zhang Z, Cai Y, et al. Enhanced performance of CH3NH3PbI3_xClx perovskite solar cells by CH3NH3I modification of TiO2-perovskite layer interface. Nanoscale Res Lett. 2016;11:316.

[42] Bhatt V, Kumar M, Yadav P, et al. Low cost and solution processible sandwiched CH3NH3PbI3_xClx based photodetector. Mater Res Bull. 2018;99:79.

[43] Li Y, Sun W, Yan W, et al. High-Performance planar solar cells based on CH3NH3PbI3_xClx perovskites with determined chlorine mole fraction. Adv Funct Mater. 2015;25:4867.

[44] Kumar P, Chauhan AK. Highly efficient flexible perovskite solar cells and their photo-stability. J Phys D: Appl Phys. 2019;53:035101.

[45] Zhao Y, M A, Nardes KZ. Effective hole extraction using MoOx-Al contact in perovskite CH3NH3PbI3 solar cells. Appl Phys Lett. 2014;104:213906.

[46] Svanstrom S, Jacobsson TJ, Boschloo G, et al. Degradation mechanism of silver metal deposited on lead halide perovskites. ACS Appl Mater Interfaces. 2020;12(6):7212.

[47] Bi D, Tress W, Dar MI, et al. Efficient luminescent solar cells based on tailored mixed-cation perovskites. Sci Adv. 2016;2(1):e1501170.

[48] Saliba M, Matsui T, Seo JY, et al. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. Energy Environ Sci. 2016;9:1989.

[49] Philippe B, Park B, Lindblad R. Chemical and electronic structure characterization of lead halide perovskites and stability behavior under different exposures-A photoelectron spectroscopy investigation. Chem Mater. 2015;27(5):1720.

[50] Jung MC, Raga SR, Ono LK, et al. Substantial improvement of perovskite solar cells stability by pinhole-free hole transport layer with doping engineering. Sci Rep. 2015;5:9863.