



Lifetime Improvement of Perovskite Solar Cell, Using a Photoactive Phase Change Material

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ABSTRACT: Perovskite Solar Cells (PSCs) are the brilliant stars of the new generation photovoltaic technologies due to their superior features of perovskite material and high Power Conversion Efficiency (PCE) that has reached up to 25.5%. Their stability is the main challenge that should be addressed for the commercialization of PSCs. The perovskite structure is decomposed to its precursor in the face of continuous light irradiation (mainly UV light), humidity, and heat. In this paper, mesoporous PSCs with structure of FTO (400 nm)/Compact TiO₂ (30 nm)/Mesoporous-TiO₂ (330 nm)/CH₃NH₃PbI₃ (270 nm)/ P3HT (30 nm)/Au (100 nm) are fabricated in an uncontrolled environment. The UV light stability of the PSC is enhanced by adding a photoactive Phase Change Material (PCM) into the perovskite. The PCM undergoes trans-to-cis isomerization under UV light irradiation. Afterwards, the cis form absorbs the heat produced in the solar cell and converts it into its trans isomer in a reversible process. By this approach, the destructive effect of UV light and heat is prohibited, leading to the enhancement of PSC durability by almost 2.4 times compared to devices without PCM. Indeed, the PCE of the device with AzB reaches 67% of the initial PCE upon 120 min of light soaking under AM 1.5, while the device without AzB only keeps 28% of its initial PCE under the same condition. It should be noted that there is no significant difference in the PCE of both solar cells.

Review History:

Received: Feb. 05, 2022

Revised: Apr. 04, 2022

Accepted: Apr. 15, 2022

Available Online: Dec. 01, 2022

Keywords:

Perovskite Solar Cell

Phase Change Material

UV light

Stability

Azobenzene

1- Introduction

The materials with the structure of AMX₃ are called hybrid perovskites. In this formula, A is a monovalent cation like CH₃NH₃I (MAI), M is a divalent heavy metal cation such as Pb, and X is a halogen. The excellent optoelectronic features of the perovskite materials have provided a PCE of 25.5% [1]. Some of the excellent optoelectronic features of the perovskite materials are high light absorption coefficient, tunable bandgap, long carrier diffusion length, and easy fabrication methods [2-4]. Despite such positive features, the perovskites are faced with problems such as degradation in confronting UV light irradiation, high humidity, and heat [5-7]. For instance, defect trap states are formed in the device layers and interfaces when exposed to UV-light [8]. Since UV light can damage the perovskite structure, much research has focused on the light stability improvement of perovskites [9-11]. For example, an effective conjugated polymer as an HTL is used as a UV filter in inverted PSCs achieving high UV light stability [12]. In another work, the UV stability of the planar CH₃NH₃PbI_{3-x}Cl_x-based PSC is effectively improved using CsBr as an interfacial layer in the ETL/perovskite interface. Conversely, some reports show that irradiation of the high-power UV light in a short time can lead to the passivation of

defect states and recovery of the damaged PSC [13, 14].

The researchers have focused on the Azobenzene (AzB) photo-switcher molecule due to its structural changes in exposure to UV light. It is an aromatic molecule with the formula of C₁₂H₁₀N₂ that isomerizes from *trans* to *cis* by UV-light exposure [15]. Moreover, the *cis* isomer is less stable than the *trans* isomer. It can be isomerized to *trans* isomer by absorbing heat or blue light [16, 17]. In this regard, the AzB has been added into the 2D perovskite interfacial layer in the previous work to increase the PCE and UV stability of the devices. Growth of 2D-perovskite in vertical orientation caused by AzB leads to a better charge transport in 2D-perovskite and enhanced Jsc, delivering higher PCE [11].

Here, we add the AzB to the perovskite precursor to enhance the lifetime of MAPI PSC against UV light. To confirm the applicable effect of AzB incorporation into perovskite, optical and structural properties of perovskite films are studied by absorbance spectra, X-ray Diffraction (XRD) patterns, and Field Emission Scanning Electron Microscope (FESEM) images. Additionally, the J-V characteristics of the PSCs are measured and compared for devices with and without AzB. Furthermore, the PSCs lifetime under continuous illumination is studied to examine the AzB effect on UV stability of PSCs.

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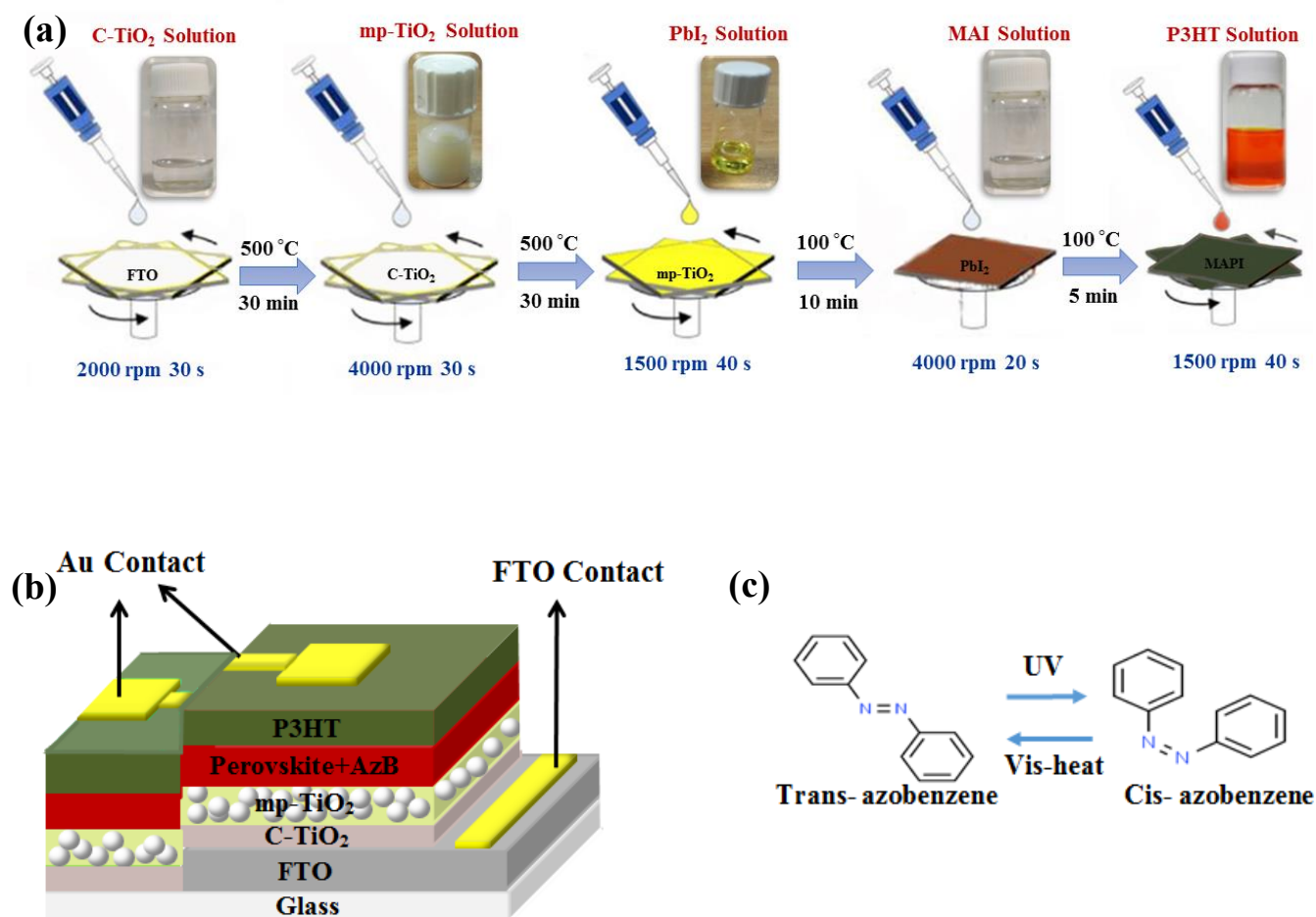


Fig. 1. The schematic of (a) preparation steps of PSC (b) the device architecture and (c) cis to trans isomerization of AzB molecule.

2- Experimental Methods

First, the Fluorine-doped Tin Oxide (FTO)- substrates are etched by hydrochloric acid and zinc powder to remove a thin strip of FTO for top gold deposition, preventing the device short circuit. Afterwards, the cleaning process is performed in sequence by soap solution, acetone, ethanol, and isopropanol under sonication each for 10 min, followed by drying at 100 °C. Fig. 1a shows the schematics of all solution preparation steps of PSC. Initially, a mild solution of TiO₂ containing tetra isopropyl orthotitanate (TTIP) in ethanol is spin-coated on cleaned FTO substrates at 2000 rpm for 30 s to deposit a TiO₂ compact (c-TiO₂) layer. After annealing the layers at 500 °C for 30 minutes in a furnace, the TiO₂ paste solution with 20 nm TiO₂ nanoparticles in ethanol (150 mg/ml) is coated on c-TiO₂ substrates at a speed of 4000 rpm for 30 s to deposit the mesoporous TiO₂ (mp-TiO₂) layer. Thereafter, the substrates are annealed at 500 °C for 30 min. The MAPI active layer is synthesized

using a two-step sequential spin coating technique. At first, the PbI₂ solution with a concentration of 1M in Dried Dimethylformamide (DMF) is spin-coated on the mp-TiO₂ substrate, quickly followed by heating at 100 °C for 10 minutes. The Methylammonium Iodide (MAI) solution (10 mg ml⁻¹ in IPA) is poured on the PbI₂ substrate, after 40 minutes of delaying, spin-coated at a speed of 4000 rpm for 20 s, quickly afterward dried at 100 °C for 5 min. For devices with AzB, 6 mg of AzB is added to the MAI solution. After that, a solution of P3HT in chlorobenzene (10 mg ml⁻¹) is spin-coated on the perovskite absorber layer at a speed of 1500 rpm for 40 s. Eventually, an Au top contact is deposited on P3HT substrates by the Physical Vapor Deposition (PVD) technique.

3- Results and Discussion

The schematic illustration of the fabricated PSC is shown in Fig. 1b, in which FTO is the bottom transparent

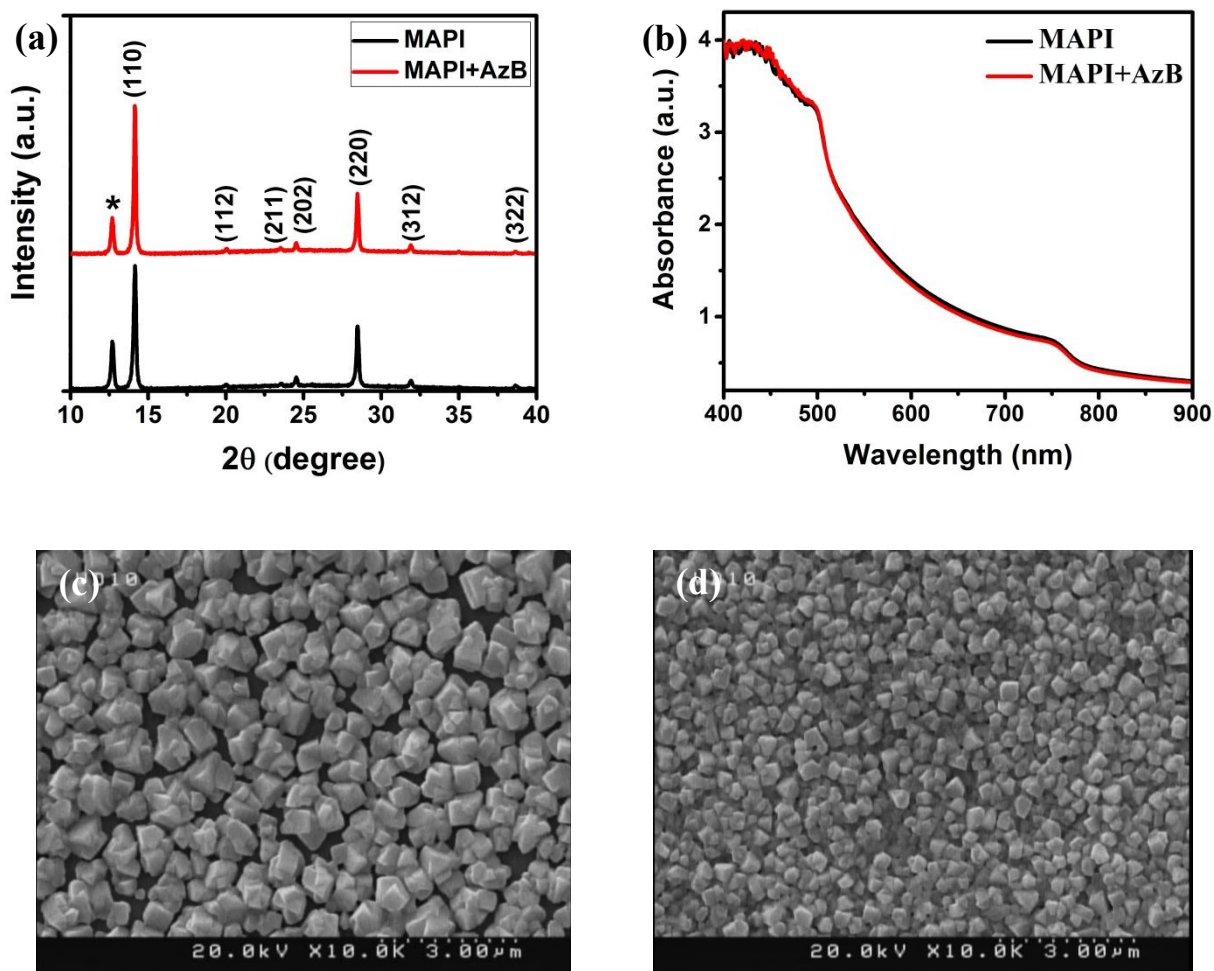


Fig. 2. (a) XRD patterns and (b) Absorbance spectra of MAPI with and without AzB, and (c) FESEM images from the surface of MAPI without and (d) with AzB deposited on glass substrates.

contact, TiO_2 is the Electron Transport Layer (ETL), and P3HT acts as a Hole Transport Layer (HTL). The formation of perovskite layers with the typical tetragonal phase is confirmed by the XRD patterns shown in Fig. 2a [18]. The diffraction peaks appeared in $2\theta=14.17^\circ$, 20.04° , 23.56° , 24.53° , 28.47° , 34.99° , and 38.59° are assigned to the (110), (112), (211), (202), (220), (312), and (322) planes, respectively [19]. The diffraction peak observed at 12.71° is attributed to the excess PbI_2 [18]. The relative intensity of the peak assigned to the (110) plane of perovskite increases with AzB incorporation, suggesting the oriented crystal growth. Seemingly, the spatial order of perovskite crystals is prepared by the planar trans isomer of AzB. According to the isomerization mechanism, heating the layers after spin coating the MAI/AzB solution also causes the *cis* to planar *trans*-isomer transform (Fig. 1c) [20].

The absorbance spectra of MAPI perovskite layers with and without AzB are shown in Fig. 2a and b. As can be illustrated, there is no change in perovskite absorption by

incorporation of AzB into MAPI.

Fig. 2c and d show the top view FESEM images of the MAPI layers with and without AzB. Cuboid-shaped grains are observed for both samples. In the presence of AzB, the layer is made more uniform since the grains are more closely packed. Therefore, AzB helps to better perovskite coverage and causes the formation of fewer pin-holes.

Comparison of the FESEM images (Fig. 2c and d) exhibits that the AzB leads to a more uniform surface coverage while reducing the grain size, and thus acted as a double-edged sword, ultimately failing to help improve efficiency. However, the purpose of this work is stability improvement of the PSC, as investigated below.

Figure 3a shows the different parts of the fabricated solar cell, with the introduction of the components. The cross-sectional FESEM image of a fabricated device is shown in Fig. 3b, clearly showing the boundary of each layer and the thickness of the layers.

Fig. 3c exhibits the J-V curves of the fabricated solar

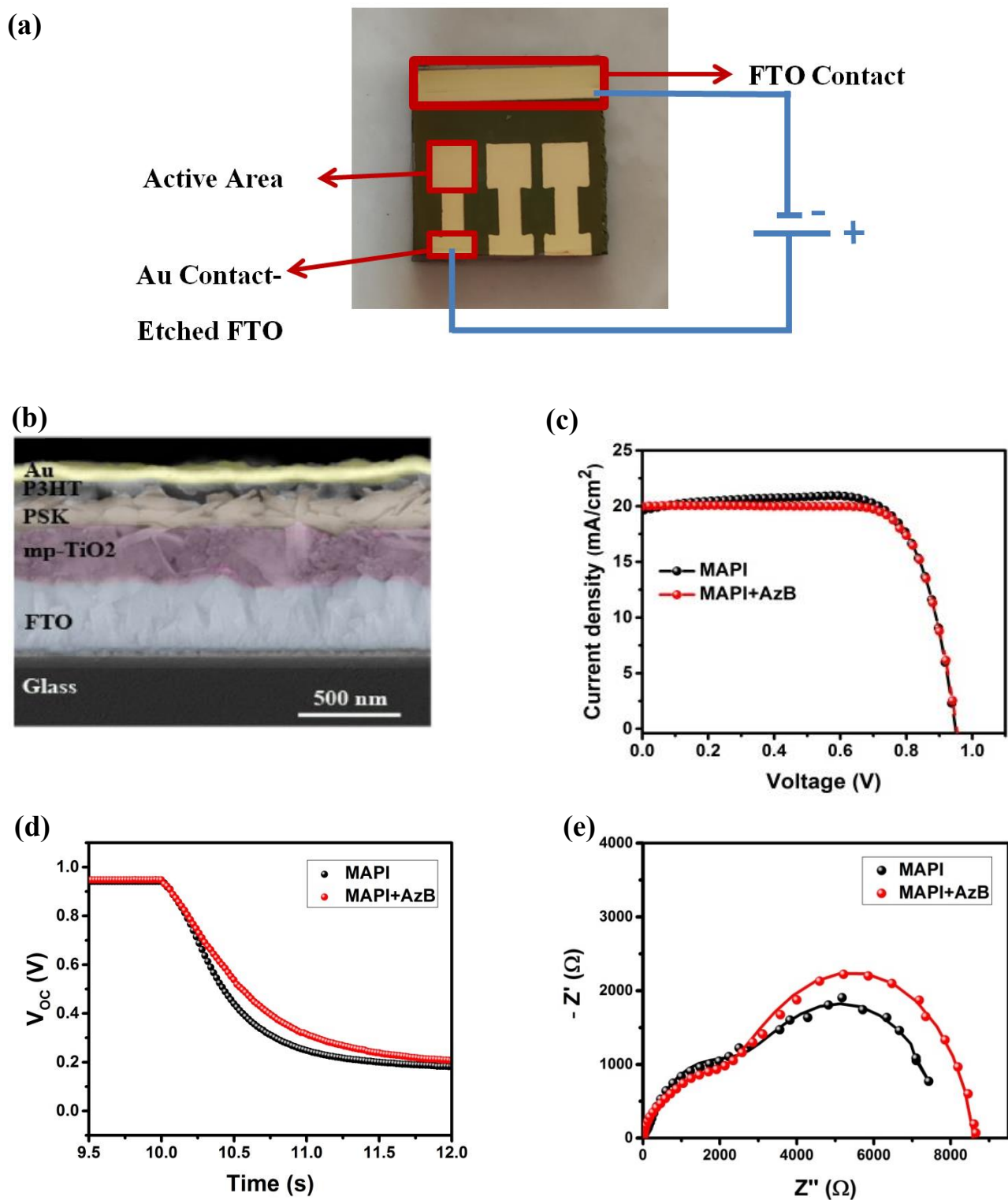


Fig. 3. (a) A photo of a completed device (top view) with the introduction of the components. (b) FESEM image from cross-section of PSC (c) The J-V curves of the devices with and without AzB under 1-sun illumination. (d) Voc decay and (e) EIS of PSCs with and without AzB.

Table 1. Photovoltaic parameters of the devices related to J-V curves presented in figure 3b.

Device	PCE (%)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)
MAPI	14.45	19.63	0.95	77
MAPI/AzB	14.26	19.99	0.96	74

cells obtained under 1-sun illumination. Table 1 outlines the photovoltaic parameters of open-circuit voltage (V_{oc}), short current density (J_{sc}), and calculated PCE and Fill Factor (FF). The results show no considerable difference in the PCE of both devices, which agrees with the absorption graphs (Fig. 2b). In contrast, in our previous work, we showed the PCE of 3D/2D perovskite-based devices surprisingly increases by adding AzB into the 2D perovskite layer, on top of the 3D perovskite [11]. It is attributed to the vertical growth of 2D-perovskite caused by AzB led to better charge transport in the 2D-perovskite and enhanced J_{sc} , delivering higher PCE.

Additionally, in another work, AzB has been added to the PbI_2 precursor solution, which decreased the solar cell efficiency [21]. However, it is shown that AzB has an effective role in increasing cell stability. Fortunately, in this paper, by adding AzB into the MAI solution and perovskite deposition in a two-step method, the device stability is boosted while keeping the efficiency constant. Additionally, in another work that Br was added to the MAI solution aiming to prolong the device stability, increasing the lifetime was achieved at the cost of losing PCE [7]. Therefore, the addition of AzB to the MAI solution, while increasing stability, does not reduce the PCE of the solar cells, showing the strength of using AzB in this work.

The V_{oc} -decay curves of the devices are recorded to examine the dynamics of photogenerated charge carriers in the PSCs. According to Fig. 3d, when the incident light is switched off, the V_{oc} of the PSCs is dropped. However, decay is slower for PSCs with AzB, indicating the longer carrier lifetime of devices containing AzB, and lower carrier recombination rate comparing the PSC without AzB. The trap states presented in an absorber layer can reduce the lifetime of the charge carriers by generating the parallel recombination pathways that speed up the recombination, leading to low charge concentration. The longer carrier lifetime of the devices with AzB compared to PSC without AzB can be due to more closed-packed perovskite grains and lower pinholes caused by AzB (Fig. 2 c and d).

For deeper investigation of devices, the Electrochemical Impedance Spectroscopy (EIS) responses are recorded for devices with and without AzB under 1-Sun illumination at zero applied voltage bias. Fig. 3e exhibited the Nyquist plots

of impedance spectra of both devices. The semi-circle that appeared in the high-frequency range is assigned to the charge transport resistance at device interfaces and gold contact. Moreover, the semi-circle located at the low-frequency range is attributed to the recombination resistance (R_{rec}) and ion diffusion and migration [22]. The higher R_{rec} of devices containing AzB (Fig. 3e) show the lower recombination rate as comparing the reference PSC, agreeing with the V_{oc} decay analysis shown in Fig 3c. Increasing the R_{rec} in the presence of AzB can be due to neutralizing the recombination centres, such as defect trap states and leakage at the perovskite interfaces and MAPI bulk. Hence, the higher V_{oc} of the device with AzB can be due to the reduced recombination rate.

The stability of unencapsulated PSCs is checked under continuous AM 1.5 light, soaking for 120 min. Under the illumination, the J-V curves are measured at 5 min intervals. Fig. 4 exhibits the higher stability of solar cells with a MAPI-AzB layer. At the beginning of light exposure, the PCE of the MAPI-AzB solar cell enhances (20%) and later falls for about 80 min of light irradiation, remaining constant afterward. After 120 min of continuous light exposure, the PCE reaches 67% of the initial PCE. However, the device with pure MAPI (without AzB) only keeps 28% of its initial PCE after 120 min of light soaking. Therefore, the destructive effect of continuous light exposure and heat is prohibited by AzB, leading to higher PSC durability by almost 2.4 times compared to devices without PCM.

The rising PCE at first light exposure can be due to the moving ion induced by light or electric field that leads to structural variations [23].

As presented in Figs. 4b and d, the V_{oc} and FF of the solar cell containing AzB increase and almost keep stable. Regarding J_{sc} , it reduces only 31% when AzB is added to the perovskite whereas for the control device it dropped to 70% of the initial value (Fig. 4c).

As mentioned earlier, the perovskite structure can degrade under UV-light irradiation [13]. As shown in Fig. 1c, AzB has two forms of planar *trans* and non-planar *cis*. By UV-light absorption, the *trans* isomer of AzB can isomerize to a less stable *cis* form, and the conversion of *cis* to *trans* isomer is made by heating or blue light exposure [24]. Therefore, by incorporation of AzB into the perovskite layer, the UV-

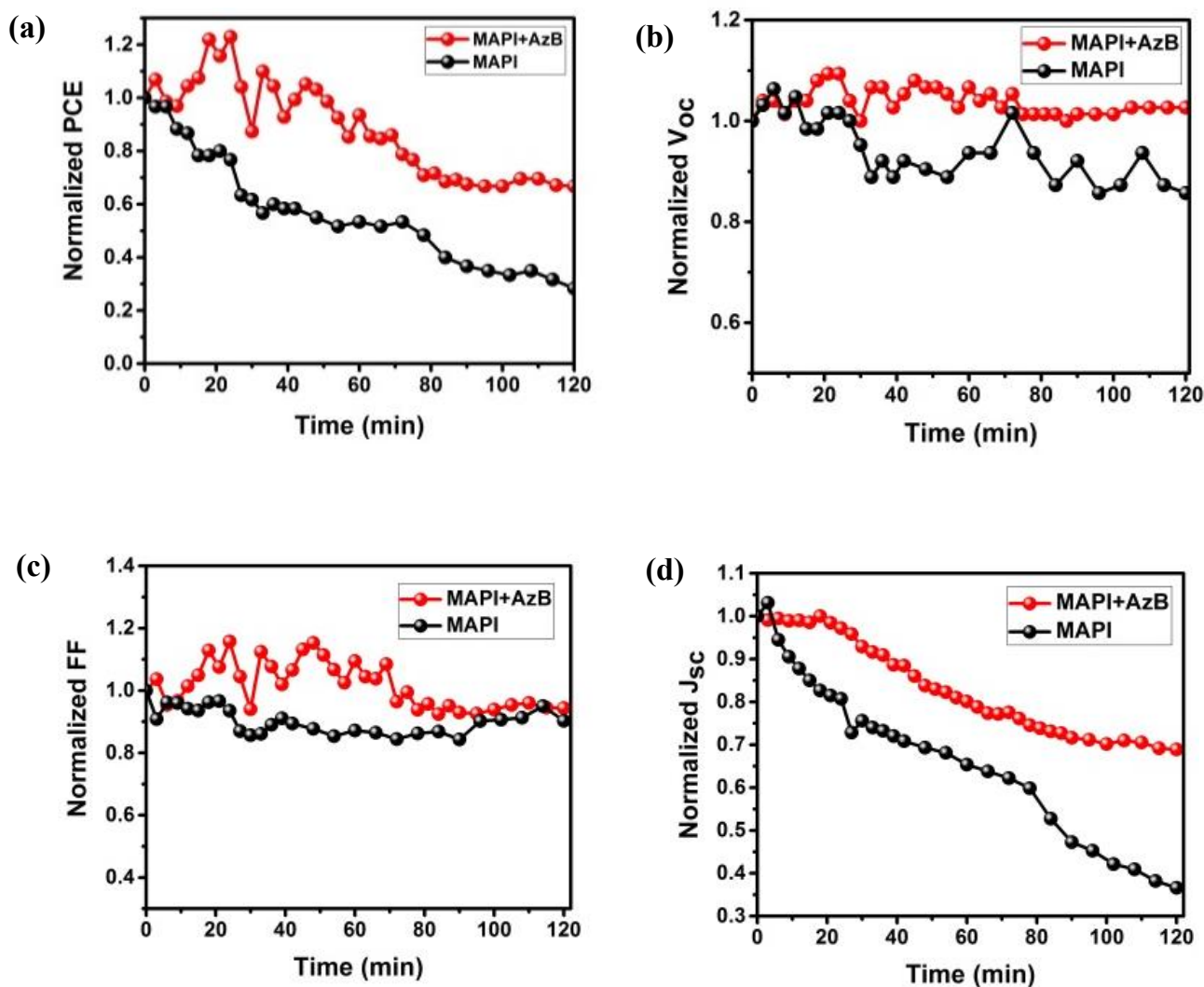


Fig. 4. The normalized PCE, Voc, Jsc, and FF of PSCs with and without AzB under 1-Sun light soaking.

light and the produced thermal energy can be consumed in the reversible thermal cis to the trans process of AzB, preventing the perovskite damaging by heat or UV light.

4- Conclusion

AzB was introduced into the MAPI perovskite absorber layer as a UV-light protector of the PSC. AzB PCM transformation from *trans* to *cis* isomers by absorbing the UV light of incident solar spectrum preventing the device damaging under the UV light, enhancing the device lifetime. The properties of the MAPI layer were examined by optical and structural analysis to capture the effect of adding AzB into perovskite on PCE and the durability of the PSCs. The tetragonal perovskite phase formation was confirmed by the XRD patterns. Additionally, the MAPI perovskite peak intensity in [110] direction was increased by adding AzB, indicating better perovskite crystallization. Furthermore, FESEM images exhibited the uniform perovskite surface with low pinhole concentration

by adding AzB into the MAPI. The PSCs lifetime was examined while exposed to a steady 1-sun simulated sunlight. The AzB effectively prolonged the PSC lifetime that kept about 66% of initial PCE after 120 min 1-sun light soaking, while the device without AzB maintained about 28% of the initial PCE.

Acknowledgements

This work was financially supported by Iran National Science Foundation (INSF). The authors would like to acknowledge the financial support received from Tarbiat Modares University, through research groups of Nano PlasmPhotonic, Grant No. IG-39703 and Phase Change Materials, Grant No. IG-39710.

Nomenclature

A	Area, m^2
V	Voltage, V

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HOW TO CITE THIS ARTICLE

M. Alidaei, V. Ahmadi, F. Arabpour, *Lifetime Improvement of Perovskite Solar Cell, Using a Photoactive Phase Change Material*, *AUT J. Elec. Eng.*, 54(2) (2022) 165-172.

DOI: [10.22060/ej.2022.21056.5450](https://doi.org/10.22060/ej.2022.21056.5450)

