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The Effect of Zn (II) Containing Metal-Organic Frameworks on Perovskite Solar Cells

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ABSTRACT

n this study, we use metal-organic frameworks (MOFs), TMU-60 ([Zn (OBA)(L*). DMF]L*=5,6-di(pyridine-4-yl)-1,2,3,4 – tetrahydropyrazine) (compound I), and TMU-60-Cd (compound II), with excellent conductivity as additives in perovskite solution. The presence of cadmium in the structure of TMU-60-Cd can significantly enhance the conductivity of the framework. These frameworks can transfer the electron between the structures. Therefore, the use of these frameworks in perovskite solar cells could have a positive effect on electron transfer. However due to the creation of a lot of voids during the formation of perovskite layer, the power-conversion efficiency (PCE) of resulting PCSs were weaker than the pristine PCS. The results revealed that using even small amounts of TMU-60, and TMU-60-Cd caused a significant reduction in PCE, and the short current densities (J_{sc}) , while improving the stability of the perovskite film, and the device. The absorption, and morphology of the new perovskite layer was also studied by UV-Vis spectroscopy, FE-SEM, and XRD. Prog. Color Colorants Coat. 14 (2021), 259-267© Institute for Color Science and Technology.

1. Introduction

In recent year, many efforts have been done to improve the performance of dye sensitizer solar cells (DSSCs), and perovskite solar cells (PSCs) by fabrication of DSSCs using Na-doped TiO₂ as photo-anode and using novel organic dyes, and for PCSs studying the effect of antisolvent dropping delay time on the morphology, and structure of perovskite films [1-3]. In general, organic-inorganic lead halide perovskite solar cells have received attention due to the great photovoltaic properties of the perovskite layers and their excellent optoelectronic specifications, such as high absorption coefficient, low exciton binding energy, and tunable energy band-gap [4-7]. But one of the challenges is and increasing the stability of the devices. The proper perovskite films can be provided using various methods such as sequential deposition [8], one-step solution process [9], anti-solvent spin-coating [10], hot-substrate [11], and additive incorporation [12]. Among them additive incorporation is one of the common ways. In which the additives can help to improve the film morphology and the crystallinity of perovskite layers. Additives mainly using in perovskite solar cells are polymers, fullerenes, metal-halide salts, inorganic acids, solvents, organic halide salts, nanoparticles, etc [13]. In the following, for modifying the film quality, the additive optimization was

achieving the proper morphology of perovskite layers,

developed, which accelerates the crystallization process, thus producing remarkably smooth and uniform perovskite films. Over the past few years, the incorporation of Metal-Organic Frameworks (MOFs) as additives in the perovskite solution has become the most common method to improve the morphology of perovskite layers, and the photovoltaic performance of PSCs. MOFs are a kind of crystalline materials prepared from metal-based nodes, and organic linker [14, 15]. They have regular nanostructured pores and high surface area [16]. MOFs have many applications in research fields such as gas storage [17], separation processes [18], chemical sensing [19], catalysis [20, 21] photocatalysis [22-25], and electrochromic thin films [26, 27]. Moreover, MOFs are employed as additives in PSCs. For example, Vinogradov et al. [28] applied Ti₈O₈(OH)₄-(O₂C-C₆H₄-CO₂)₆ (MIL-125) in electron transport layer to enhance the stability of the device. Chang et al. [29] used MOF-525 as additive in the perovskite solution and investigated its effect on the improvement of crystallinity of perovskite film. Shen et al. [30] employed C₈H₁₀N₄Zn (ZIF-8) for improving the crystallization, and the photovoltaic property of PSCs. Li et al. [31] examined a 3D MOF [In₂(phen)₃Cl₆].CH₃CN.2H₂O(In2) as additive into the hole transport layer. They also employed this 3D MOF into lead iodide solution to modify the performance of the perovskite layers [32].

Here, we used MOFs as additives in the solutionprocess. We also applied one-step process for preparation of perovskite layer by solvent-engineering technique, because it is a proper procedure for fabrication of efficient lead iodide perovskite structures [10].

TMU-60 [Zn (OBA) (L*).DMF] (compound I), L^{*}= 5,6- di (pyridine-4-yl)-1,2,3,4-tetrahydropyrazine, and TMU-60-Cd (compound II) were used, as additives in PSCs, because these frameworks have recently shown high electrical conductivity. For example, the presence of cadmium increased the conductivity from 53×10^{-6} to 1.8×10^{-2} S.cm⁻¹ in compressed pellet at room temperature for TMU-60, and TMU-60-Cd respectively [33].

Generally, according to the articles, the addition of metal organic frameworks can modify the band gap energy and increase the specific surface area of the resultant materials. Moreover these compounds as adsorbent, increased the charge transport and decreased charge recombination. As a result, these additives were employed for the enhancement of short circuit current density (Jsc), stability of cells, and appropriate conduction band position.

2. Experimental

2.1. Materials and analysis

All of the chemical reagents for the synthesis of additive and analysis were commercially available from Merck Co. They were used directly without purification. Materials for the fabrication of solar cells such as TiO₂ paste, PbI₂ CH₃NH₃I, and spiro were purchased from Sharif Solar Company. All materials for the synthesis of CH₃NH₃PbI₃ solution (in DMF & DMSO) for one-step spin-coating, and diethyl ether for solvent-engineering techniques were purchased from Merck Co. FT-IR spectrum was recorded on a Brukertensor 27 spectrophotometer by using KBr disk technique in the range of 400-4000 cm⁻¹. Absorption spectra of the perovskite layers were recorded by a Shimadzu UV-3103 UV-Vis spectrophotometer. The phase purity, and crystalline structure were examined using powder X-ray diffraction (XRD) technique INEL Equinox (X'Pert Pro, 3000, X-ray diffractometer) at room temperature with Cu-K α (λ = 1.54 Å) radiation. The crystallite sizes of the perovskite film was calculated using the Scherrer-formula. Tescan Mira FE-SEM and energy dispersive X-ray (EDX) instrument were used to study the surface morphology of the perovskite films. Current-voltage (I-V) curves were measured under simulated sunlight instrument, and air mass 1.5 G illumination (Palmsens) Sharif Solar, Iran. EIS measurements were performed using an electrochemical workstation (Autolab 302N) in the frequency range of from (100kHz-100mHz).

2.2. Synthesis of [Zn(OBA) (L*)]·DMF (TMU-60)

TMU-60 was synthesized according to our previous research [33]. In summary, 0.5 mmol of L ligand was dissolved in DMF for 5 min. Then, 0.05 g sodium cyanide was added to the solution. The solution was heated to 120 °C for 20 min. After evaporation of the solvent, the remaining sediment was washed with ethanol.

Mp: 70.2 °C. IR (KBr, cm⁻¹): 3301 (s), 3032(m), 2843(s), 1667(m), 1595(s), 1406(s), 1318(w), 1218(w), 1095(w),992(w), 823(m), 586(m). (¹H NMR (500 MHz,

DMSO): δ 10.3 (d, 2H,-NH), 8.3 (d, 4H, ArH), 7.61 (d, 4H, Ar-H), and 3.9 (s, 4H, HC-C). Elemental analysis (%) calculated: C 67.27, H 6.59, N 26.15. The mass and ¹H NMR spectrum of L* ligand are presented [33].

2.3 Device fabrication

Fluorine-doped Tin Oxide (FTO) (15 Ω /square) with coated glass substrates were cut into 1.5×1.5 cm sizes. For the preparation of the half-cell, one piece of FTO glass was etched by Zn powder in 6 M HCl solution and, then cleaned by sonication in acetone, dilute solution of HCl, ethanol, isopropyl alcohol, and DI water for 10 min, followed by annealing at 500 °C for one hour. To form a thick TiO₂ blocking layer, diluted titanium isopropoxide solution in ethanol was, spin-casted (1000 rpm, 30 s) onto FTO substrate. Then, they were annealed at 500 °C for one hour. A mesoporous TiO₂ layer (m- TiO_2) was deposited by spin coating for (4000 rpm, 20 s). These layers were immediately and quickly annealed at 100 °C for 10 min, and then sintered at 450 °C for 30 min. Perovskite precursor CH₃NH₃PbI₃ was obtained by 462 mg PbI₂, and 159 mg CH₃NH₃I in 1 mL mixed solvent of DMF: DMSO= 4:1 (volume ratio), with solvent engineering techniques and depositing by spin coating (4500 rpm, 30 s). During spin-coating, 150 µl diethyl ether was poured on the substrate every 12 s [10]. Then, the substrate was annealed at 100 °C for 10 min. Subsequently, the hole transport layer (Spiro-MeOTAD), was deposited by spin-coating (3000 rpm, 30 s). Finally, Au was evaporated on the perovskite layer to produce a PSC device.

To evaluate the stability of the electrochemical performance of the cells, they were kept under ambient conditions for 20 days after which the current and voltage of the cells, were measured again to evaluate the stability of the cells.

3. Results and Discussion

3.1. Characterization of perovskite solar cells

This research, focused on the effect of different percentages of TMU-60 (compound I) and TMU-60-Cd (compound II) on the properties of perovskite film and devices such as film morphology, light absorption, and device performance. To examine the effect of compounds I and II MOFs, their nanoparticles were synthesized, and employed as additives on performance of PSCs. At the beginning of the work, CH₃NH₃PbI₃ solutions (CH₃NH₃PbI₃ in DMF and DMSO) with different amounts of compounds I and II were prepared and used for fabrication of PSCs. We employed compounds I and II nanoparticles by solventengineering technique in one-step deposition of solution (CH₃NH₃PbI₃ with compounds I and II in DMF & DMSO) to prepare the perovskite layer. The performance of PSCs devices based on CH₃NH₃PbI₃ with optimal amounts of compounds I and II are shown in Figure 1a, and Table 1. The results show that the solar cell with 2% compounds I and II have acceptable results in short-circuit current density (Jsc), and power conversion efficiency (PCE). In contrast, better results were obtained with the cell without additive (pristine). Moreover, in cells with compound II, the results were less than the others. Compound II caused the reduction of short current density (J_{sc}) , open-circuit voltage (V_{oc}) , and PCE. As a result, by adding compounds I and II nanoparticles to perovskite precursor solution and during the synthesis by thermal processes, a lot of voids created in perovskite layer, that led to the phase separation, resulting the reduction of J_{sc} and PCE.

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No	Additive in perovskite precursor solution	J _{sc} (mA/cm ²) ¹	$\overline{V_{oc}}(V)^2$	FF ³	η (%) 4	
					After preparation	after 20 days
Ι	0 wt % of additive	13.9	1.0	0.65	9.0	3.4
II	2 wt % of compound I	11.4	0.97	0.66	7.3	3.9
III	2 wt % of compound II	9.9	0.97	0.69	6.6	4.9

 ${}^{I}J_{SC}$ (mA cm⁻²) is the short-circuit current density.

 $^{2}V_{OC}$ (V) is the open-circuit voltage.

 ${}^{3}FF$ is the fill factor.

 ${}^{4}\eta$ (%) = $(J_{SC} \times V_{OC} \times FF)/P_{in}$ where P_{in} is the incident light.

The reference (pristine) device without additive showed V_{oc} of 1.0 V, J_{sc} of 13.9 mA/cm², FF of 0.65, and PCE of 9.0 %. However, compound I decreased PCE (from 9.0 to 7.3), because J_{sc} decreased from 13.9 to 11.4 mA/cm². Compound II also resulted in the, reduction of PCE from 9.0 to 6.6 % that it is smaller than the compound I (Table 1). Moreover, the PCE of the pristine device changed from 9.0 to 3.4 (62.2 % change) after 20 days under ambient condition, while that of the device with compound I decreased from 7.3 to 3.9 (46.6 % change) and for the compound II changed from 6.6 to 4.9 (26 % change). The performance of PSCs devices based on CH₃NH₃PbI₃ with optimal amounts of compounds I and II after 20 days under ambient conditions are shown in Figure 1a and 1b. It is quite obvious that the intensity of the current and the potential, and consequently, the efficiency have been significantly reduced in pristine cell after 20 days. While in cells made with additive, the results after 20 days are better than the pristine cell. Also, compared to Figure 1a, it can be seen that the current and potential in the pristine cells fell significantly compared to the first day.

As a result, by adding compound II, less decrease in PCE occurred under ambient conditions, with better stability than the pristine cell. This agrees with the results of XRD which are described below.

Figure 2 represents the CH₃NH₃PbI₃ top-view SEM images of the devices with and without additives. Figure 2(a) exhibits the layers without additives (pristine), while Figure 2(b) and 2(c) illustrate top-view SEM images of (2 % wt of compound I, and compound II). As shown in Figures 2(a) to 2(c), the surface morphology of perovskite film without additive is regular and without pinholes with uniform coverage in comparison to others. When the amount of compounds I and II was added, perovskite layers were formed with larger grain sizes but numerous pinholes created in them. So, SEM images revealed that the compact CH₃NH₃PbI₃ film with uniform coverage could be achieved without additive. EDX analysis of perovskite layers in Figure 3 clearly shows the existence of compounds I and II in the perovskite layers and confirms the presence of zinc and cadmium elements.



Figure 1: J-V curves of CH₃NH₃Pbl₃ PSC devices with or without additive measured under illumination of an AM 1.5 solar simulator (100 mW cm⁻²) in air a) after preparation and b) after 20 days. The scanning direction is from open-circuit voltage to short circuit.



Figure 2: FE-SEM micrograph of the a) CH₃NH₃Pbl₃ without additive (pristine perovskite film), b) with 2 % wt % of compound I and c) with 2 % wt % of compound II.



Figure 3: EDX analysis of a) pristine perovskite layer, b) perovskite layer with compound I and c) perovskite layer with compound II.

Figure 4 shows XRD patterns of the $CH_3NH_3PbI_3$ layers to check the effect of additive on the morphology and crystallinity after addition of compounds I and II. All XRD peaks at 20 value of 14.2°, 19.9°, 24.5°, 26.5°, 31.8°, and 40.6° indicate the prepared films have a tetragonal crystal structure. The lead methyl ammonium iodide perovskites can have 3 different crystalline phases, which are temperature-dependent: orthorhombic, tetragonal and cubic [34].

Thus, despite the presence of compounds I and II, perovskite has been effectively formed. X-ray diffraction (XRD) was also used to measure the crystallite sizes of perovskite layers with the Scherrer equation (Eq. 1) [34, 35].

$$d = \frac{(0.891\,\lambda)}{\cos\theta_B \cdot \left[(B_{sample}^2 - B_{reference}^2)^{0.5}\right]} \tag{1}$$

Where, d is the crystallite size, β is the full width at half maximum (FWHM) of diffraction peak in radians, λ is the wavelength, and θ is the diffraction angle.

Other peaks at 26.5, 37.9 and 51.7 correspond to FTO layer. By assuming the most intense peaks at $2\theta = 14.2$, the calculated average crystalline size of the perovskite layer was 49.44 nm (for pristine), 54.88 nm (for compound I), and 96.35 nm (for compound II). As a result larger perovskite crystals have been formed in the presence of additives. Particularly, by the addition of compound II, the grain size of crystals increased,

that improved the stability of perovskite film. Moreover, in Figure 4, the film without additive shows a peak at 12.6° related to PbI₂ (001), which indicates partial decomposition or unreacted PbI₂ in perovskite film. As a result, the intensity of PbI₂ peak decreased by adding compounds I and II. However, in the perovskite layer containing compound II, this peak disappears completely. It is evident from Figure 4(b) and 4(c) that the presence of compounds I and II has a positive effect on the stability of the perovskite layer.

We employed UV-Vis absorption spectroscopy to determine the absorption range and intensity of perovskite films (Figure 5). The diagram shows that the absorption of the perovskite layer in the presence of additive has almost changed. The pristine layer absorption shows the excitation peak between 400 to 450 nm, and the onset of absorption is in the range of 700-800 nm. The light absorption of perovskite films with additives are inconsistent with pristine film, maybe due to the presence of voids that affect the light absorption. These results are confirmed by the corresponding Jsc and PCE data in Table 1. Figure 6 shows the Nyquist plots of perovskite with and without additives under AM1.5 sun illumination. The resistance of layers increase for the layers with additives compared to pristine film. It indicates that the defects in the perovskite film were increased by the addition of additives, leading to inferior cell performance and more recombination.



Figure 4: The X-ray powder diffraction pattern of a) CH₃NH₃PbI₃ film without additive (pristine perovskite film), b) with 2 % wt % of compound I and c) with 2 % wt % of compound II.



Figure 5: UV-Vis absorption spectra of a) pristine perovskite film, b) with 2 % wt % of compound I and c) with 2 % wt % of compound II



Figure 6: Nyquist plots of a) pristine perovskite film, b) with 2 % wt % of compound I and c) with 2 % wt % of compound II

4. Conclusions

In conclusion, metal-organic frameworks (MOF), TMU-60 ($[Zn(OBA)(L^*).DMF]L^* = 5,6$ -di(pyridine-4yl)-1,2,3,4-tetrahydropyrazine) (compound I), and TMU-60-Cd (compound II) were used as additive in perovskite solar cells. XRD patterns only showed the perovskite phase. EDX analysis revealed the presence of additives as the main components in the perovskite film. EIS analysis showed that the resistance of pristine cell is lower than that of other cells. So, using additives decreased the short current density (J_{sc}) and power-conversion efficiency (PCE). Moreover, the morphology of the new perovskite layer was studied by FE-SEM, and XRD. As a result, additive improved the grain size of perovskite film on the TiO₂ layer that contributed the growth of perovskite crystals and

improved the quality of pervoskite film formation. This study showed, despite the presence of a metal-organic framework, efficiency is reduced but the stability of the devices is increased.

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