

Enhanced Performance of Perovskite Solar Cell via Controlling Layer Thickness

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ABSTRACT

In this study, Perovskite material methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) was successfully fabricated using a two-step sequential solution deposition method. The precursor solution of lead iodide was first spin-coated, followed by immersing the film into a solution of $\text{CH}_3\text{NH}_3\text{I}$ to form the Perovskite layer. The Perovskite material was then successfully applied as a light-harvesting material in Perovskite solar cells. The power conversion efficiency of the devices was optimized by varying TiO_2 blocking layer, TiO_2 mesoporous layer, and perovskite capping layer thickness. The best Perovskite solar cell exhibits a power conversion efficiency of 7.72% with a short-circuit photocurrent density J_{SC} of 17.26 mA/cm^2 , an open-circuit photovoltage V_{OC} of 0.94 V, and a fill factor of 47.6%; with the thicknesses of TiO_2 blocking layer, TiO_2 mesoporous layer, and perovskite capping layer of 100 nm, 200 nm, and 400 nm, respectively. The results show that Perovskite material has potential for solar cell application.

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1. Introduction

Over the past decade, Perovskite solar cells (PSCs) have attracted extensive attention from scientists and researchers as the next-generation photovoltaic devices to replace traditional Silicon solar cells [1]-[5]. Perovskite refers to any material with a crystal structure similar to calcium titanium oxide (CaTiO_3) [6]. Perovskite materials are classified into two main groups: inorganic oxide perovskites and halide perovskites. For photovoltaic applications, the most commonly used materials are organometal halide perovskites, such as methylammonium lead trihalide ($\text{CH}_3\text{NH}_3\text{PbX}_3$) [4], [7].

The first PSC was successfully fabricated in 2009 by the Miyasaka group with a power conversion efficiency (PCE) of 3.8% [8], however, the device was unstable due to the leakage and evaporation of the volatile liquid electrolytes that limit their commercial application. Many efforts have been made to replace the liquid electrolyte with a solid hole transport material, leading to the formation of an all-solid-state Perovskite photovoltaic device with the highest reported performance of 25.8% up to now [9].

The standard structure of mesoscopic Perovskite solar cell is illustrated in Figure 1 [10].

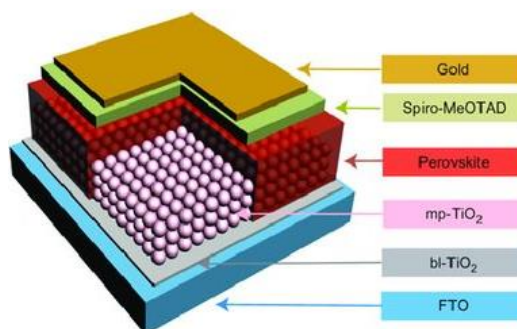


Figure 1. Mesoscopic structure of Perovskite solar cell

The device is composed of a compact TiO₂ blocking layer to diminish the recombination process occurring in the device under working conditions, a mesoporous TiO₂ layer acts as an electron transporter, with perovskite material infiltrated inside the pore and capped on top of the mesoporous TiO₂ layer as a light absorber, a hole transport layer (HTL), and a metal back contact [11], [12].

In this study, the PCE of the devices was optimized by controlling TiO₂ blocking layer thickness, TiO₂ mesoporous layer thickness, and perovskite capping layer thickness. The effects of each layer on the performance of PSCs are also discussed.

2. Materials and Methods

2.1. Materials

All chemicals in this study were used as received: hydroiodic acid (Aldrich), methylamine (TCI), acetonitrile (Aldrich), chlorobenzene (Aldrich), 1-butanol (Aldrich), zinc powder (Aldrich), titanium diisopropoxide bis(acetylacetonate) (Aldrich), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Alfa Aesar), (2,2',7,7'-tetrakis (*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (spiro-MeOTAD, TCI), and 4-*tert*-butylpyridine (*t*BP, Aldrich). Methylammonium iodide (CH₃NH₃I or MAI) was prepared according to the reported procedure [13]. In general, hydroiodic acid (30 mL, 0.227 mol) and methylamine (27.8 mL, 0.273 mol) were stirred for 2 h in an ice bath, the mixture was then evaporated at 50 °C for 1 h. The collected precipitate was washed three times with diethyl ether and dried under a vacuum for 12 hours.

2.2. Devices fabrication

The FTO (fluorine-doped tin oxide) substrates were cleaned using an ultrasonic bath with deionized water, ethanol, and acetone. The cleaned substrates were then etched using zinc powder and hydrochloric acid solution to avoid direct contact between the working electrode and the counter electrode. A compact TiO₂ blocking layer was spin-coated (2000 rpm, 30 s) onto cleaned FTO substrate using a solution of 0.15 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol, followed by heating at 125 °C for 5 min to allow the evaporation of the solvent. The films were then cooled down to room temperature and a similar process was repeated two, three, or four times using a solution of 0.3 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol. The resulting coated films were annealed at 450 °C for 30 min. After the compact TiO₂ layer was prepared, a mesoporous TiO₂ layer was sequentially deposited by spin-coating a slurry of commercial TiO₂ particles diluted in ethanol. The speed of the spin-coating process varies from 2000 to 2600 rpm to control the layer thickness. The mesoporous TiO₂ films were sintered at 450 °C for 30 min and cooled down to prepare for the deposition of perovskite films. The perovskite layers were prepared using a two-step sequential deposition method. The prepared films were infiltrated by spin-coating a PbI₂ solution in DMF at 2000 rpm for 30 s. The concentration of this solution varies from 0.8 M to 1.1 M. The resulting films were annealed at 100 °C and immersed in a solution of MAI in 2-propanol (10 mg.mL⁻¹) for 5 min. After being rinsed with 2-propanol to remove the excess salt, the films were annealed again at 100 °C. Next, the hole transport layer was deposited on top of the perovskite films by spin-coating method (2000 rpm, 30 s), with a solution of spiro-MeOTAD (0.068 M), LiTFSI (0.018 M) and *t*BP (0.05 M) in the mixed solvent of the chlorobenzene and acetonitrile. Finally, the back contact (Au) was deposited on top of the device using the thermal evaporation method. The process was carried out in a high vacuum system to obtain a 100 nm-thick layer.

The active cell area is 0.12 cm² (0.3 cm x 0.4 cm). The measurement of the device's performance was performed using a black mask to prevent overestimation in power conversion efficiency caused by scattered or reflected light [14].

2.3. Characterizations

Cross-sectional and top-view images were captured using a Hitachi S-4800 scanning electron microscope (SEM). Photovoltaic characterization was performed under standard global conditions (AM 1.5G) simulated sunlight (PEC-L11, Pecell Technologies, Inc.). Current-voltage characteristic of the device was measured using a solar simulator (AM 1.5G). The overall PCE of a solar cell is calculated

using the following equation: $PCE = \frac{J_{sc}V_{oc}FF}{P_{in}}$ where J_{sc} is the short-circuit photocurrent density, V_{oc} is the open-circuit photovoltage, FF is the fill factor, and P_{in} is the incident light intensity [15], [16].

3. Results and Discussion

3.1. Effect of number of coatings compact TiO₂ blocking layer (BL)

In this experiment, the thickness of compact TiO₂ BL was controlled by varying the number of coatings. The TiO₂ BL was coated two, three, and four times (named 2BL, 3BL, and 4BL, respectively) since the one-time coating is unable to cover the entire FTO surface. The J-V characteristics of the PSCs are shown in Fig. 2, and the corresponding numerical parameters are listed in Table 1.

Table 1. Photovoltaic parameters of PSCs with different numbers of TiO₂ BL coatings under AM 1.5G conditions.

Number of spin-coatings	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
2BL	11.19	0.56	19.31	1.21
3BL	14.13	0.84	43.55	5.17
4BL	12.09	0.77	33.65	2.94

In PSCs, the compact TiO₂ BL is used to prevent direct contact between perovskite and FTO substrate. Without this layer, the holes existing in perovskite and HTM can recombine with the collected electrons at the FTO surface. By varying the number of coatings, the thickness and density of the deposited films increase. As a result, the device with 3BL shows higher performance (5.17% in PCE with J_{sc} of 14.13 mA/cm², V_{oc} of 0.84 V, and FF of 43.55%) than the device with 2BL (1.21% in PCE with J_{sc} of 11.19 mA/cm², V_{oc} of 0.56 V, and FF of 19.31%). Further increases in the number of spin-coated times do not lead to enhanced performance, as shown by the result of the device with 4BL (PCE is 2.94% with J_{sc} of 12.09 mA/cm², V_{oc} of 0.77 V and FF of 33.65%). According to the literature, the BL should be as thin and dense as possible, since a thick layer causes higher resistance, thus lowering the electron collection of the device [17]. Another possible reason is that increase in the thickness of BL may reduce the optical transparency of the substrate, consequently, reducing the light-harvesting property of the perovskite layer. Although in planar PSCs, the compact BL may be omitted and the device still operates effectively, in mesoscopic PSCs the important role of this layer cannot be neglected. Under our spin-coating condition (2000 rpm, 30 s), the highest PCE was obtained for the device with 3BL.

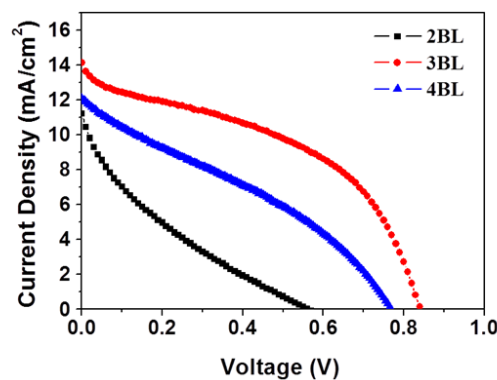


Figure 2. J-V characteristics of PSCs with different numbers of TiO₂ BL coatings under AM 1.5G conditions

3.2. Effect of TiO₂ ML and perovskite CL thickness

From the previous results, the compact TiO₂ layer spin-coated 3 times was applied for the following experiment. The TiO₂ ML is spin-coated onto the FTO-coated 3BL films using a mixture of TiO₂ particles diluted in ethanol at different spin speeds: 2000 rpm, 2200 rpm, 2400 rpm, and 2600 rpm. The first purpose is to control the TiO₂ ML thickness. By adjusting the spin speed, however, not only the

thickness of TiO₂ ML but also the thickness of perovskite CL varies, resulting from the same amounts of PbI₂ and MAI used for all devices. As presented in Fig. 3, the thinner TiO₂ ML is, the thicker perovskite CL becomes. Under spin-coating at 2000 rpm, a 240 nm-thick ML and a 500 nm-thick perovskite CL were obtained. The thicknesses of these two layers are 200 nm and 600 nm for the sample spin-coated at 2200 rpm; and 180 nm and 650 nm for the sample spin-coated at 2400 rpm.

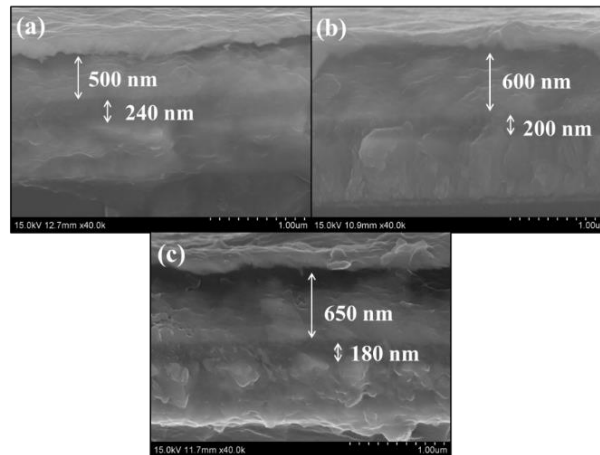


Figure 3. Cross-sectional SEM images of mesoporous TiO₂ films spin-coated at different speeds: (a) 2000 rpm, (b) 2200 rpm, and (c) 2400 rpm.

Fig. 4 and Table 2 show the photovoltaic performances of PSCs prepared at different conditions as mentioned above. It is suggested that the thickness of TiO₂ ML in mesoscopic PSCs is about 100 – 300 nm for best electron collection since the calculated diffusion length of MAPbI₃ is about 1 μm. The best device, which was spin-coated at 2200 rpm, produces a PCE of 5.17% with a J_{SC} of 14.13 mA/cm², V_{OC} of 0.84 V, and FF of 43.55%.

Table 2. Photovoltaic parameters of PSCs with TiO₂ ML spin-coated at different speeds under AM1.5G conditions.

Spin-speed	ML thickness (nm)	CL thickness (nm)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
2000 rpm	240	500	11.7	0.87	41.49	4.22
2200 rpm	200	600	14.13	0.84	43.55	5.17
2400 rpm	180	650	10.36	0.86	35.74	3.19
2600 rpm	---	---	10.06	0.8	29.82	2.4

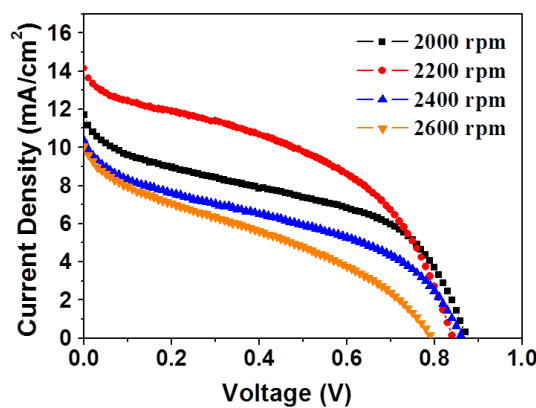


Figure 4. J-V characteristics of PSCs with TiO₂ ML spin-coated at different speeds under AM 1.5G conditions

3.3. Effect of PbI_2 concentration

The effect of perovskite CL on the performance of the device was re-evaluated by changing the concentration of the PbI_2 solution, ranging from 0.8 M to 1.1 M. All other processing conditions were kept the same as the previous experiment, except the speed for spin-coating TiO_2 ML was fixed at 2200 rpm. Table 3 and Fig. 5 illustrate the photovoltaic parameters and the corresponding J-V curves of the PSCs.

Table 3. Photovoltaic parameters of PSCs prepared with different concentrations of PbI_2 under AM 1.5G conditions.

PbI_2 /DMF concentration	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
0.8 M	13.79	0.74	38.03	3.88
0.9 M	17.26	0.94	47.6	7.72
1.0 M	15.62	0.83	43.84	5.68
1.1 M	14.83	0.71	36.88	3.86

It is commonly known that the increase in the concentration of precursor solution usually leads to an increase in resulting film thickness in the spin-coating process [18]. The thickness of the perovskite layer strongly affects the PCE of the PSCs, since perovskite plays an important role as light-harvesting material. The perovskite layer should be thick enough for efficient light collection, but a too-thick layer may hinder the charge-collecting ability of the device because electrons and holes can recombine before reaching the electrode. In addition, the resistance of a device containing a thicker film is higher than that containing a thinner one. The PSC prepared with 0.8 M PbI_2 precursor solution shows a PCE of 3.88%, whereas the devices using higher concentration show higher performance; for example, the PCE of the devices prepared with 0.9 M and 1.0 M PbI_2 solution are 7.72% and 5.68%, respectively. Further, an increase in the concentration of PbI_2 precursor solution may lead to the formation of too-thick perovskite films, consequently, reducing the PCE of the cell.

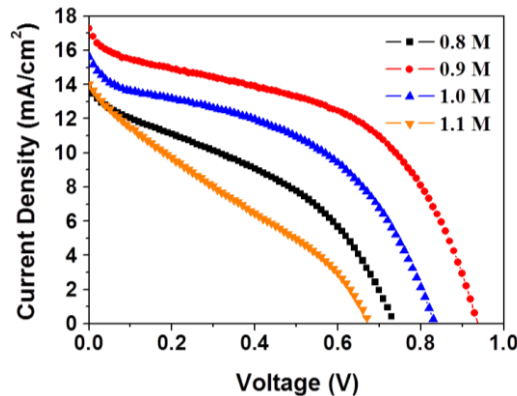


Figure 5. J-V characteristics of PSCs prepared with different concentrations of PbI_2 under AM1.5G conditions

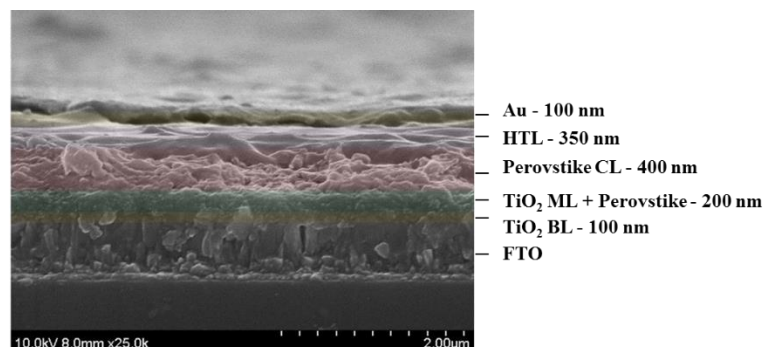


Figure 6. Cross-sectional SEM image of a complete PSC including the thickness of each layer

In this experiment, the PSC with a perovskite CL thickness of 400 nm gives the highest efficiency of 7.72%, with J_{SC} of 17.26 mA/cm² and V_{OC} of 0.94 V. Nevertheless, the FF is still lower than expected, probably due to the low uniformity of the layers. Fig. 6 shows the cross-sectional SEM image of the best device; the thickness of each layer is presented.

4. Conclusions

In this study, perovskite material MAPbI₃ was successfully prepared and applied in PSCs as light-harvesting material. The performances of PSCs were optimized by controlling the thicknesses of TiO₂ BL, TiO₂ ML, and perovskite CL. The results show that the thickness of each layer significantly affects the PCE of the devices. The best sample gives a PCE of 7.72%, with J_{SC} of 17.26 mA/cm², V_{OC} of 0.94 V, and FF of 47.6%. The thickness of TiO₂ BL, TiO₂ ML, and perovskite CL is 100 nm, 200 nm, and 400 nm, respectively. Further research on interface engineering needs to be conducted to improve the performance of the photovoltaic device.

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