

The Influence of $\text{CH}_3\text{NH}_3/\text{PbI}_2$ Ratio on The Absorption and Electrical Characteristics of Perovskite/Polymer Solar Cell

Shobih^{1,*}, Erlyta Septa Rosa¹, and Endang Lestari²

¹Research center for Electronics and Telecommunication Indonesian Institute of Sciences
Kampus LIPI Gd. 20 Jalan Sangkuriang Bandung 40135 West Java Indonesia

²Faculty of Mathematics and Natural Sciences Sebelas Maret University

Jl. Ir. Sutami No. 36A, Solo 57126 Jawa Tengah Indonesia

* Corresponding author, tel/fax: 022-2504661/2504659, email: sho99bih@gmail.com

Co-author 1, email: erlytasr@gmail.com

Co-author 2, email: endanglestari46@gmail.com

ABSTRACT

In this paper, we report a simple solution processed perovskite/polymer solar cell using $\text{CH}_3\text{NH}_3\text{PbI}_3$ as an absorber, PCBM (6,6 phenyl C61-butyric acid methyl ester) as an electron transport layer, and PEDOT:PSS (poly (3,4-ethylene dioxy thiophene):poly(styrene sulfonate)) as a hole transport layer. The absorber solution was prepared by mixing of $\text{CH}_3\text{NH}_3\text{I}$ (methyl ammonium iodide) with PbI_2 (lead iodide) in DMF (dimethyl formamide) solvent. The absorber, electron transport, and hole transport layers are deposited by spin coating of the solutions. In order to obtain the optimum optical and electrical characteristics, the mixture of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 are varied by the molar ratio of 1:1, 1:3, and 3:1, respectively. Because of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer degrades, the fabricated cells have low performance. However, the cell using a molar ratio of 1:1 $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 gives the best electrical characteristics, results in an open circuit voltage of 0.04 V, a short circuit current density of 0.08 mA/cm², and a power conversion efficiency of 0.002 %.

Keywords: perovskite solar cell, $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{I}$, PbI_2 , PCBM, PEDOT/PSS

ABSTRAK

Di dalam tulisan ini kami melaporkan proses pembuatan sel surya berbasis perovskite/polimer yang diproses dalam bentuk larutan. Sel surya perovskite/polimer menggunakan $\text{CH}_3\text{NH}_3\text{PbI}_3$ sebagai lapisan penyerap cahaya, PCBM (6,6 phenyl C61-butyric acid methyl ester) sebagai lapisan transport elektron, dan PEDOT:PSS (poly (3,4-ethylene dioxy thiophene):poly(styrene sulfonate)) sebagai lapisan transport hole. Larutan penyerap cahaya dibuat dengan mencampurkan $\text{CH}_3\text{NH}_3\text{I}$ (metil amonium iodida) dan PbI_2 (timbal iodida) dengan pelarut DMF (dimetil formamida). Lapisan-lapisan penyerap cahaya, transport elektron, dan transport hole dibuat dengan cara mendeposikan larutan-larutan tersebut menggunakan metoda spin coating. Untuk mendapatkan karakteristik listrik dan optik yang optimum campuran $\text{CH}_3\text{NH}_3\text{I}$ dan PbI_2 divariasikan dengan perbandingan molar masing-masing 1:1, 1:3, dan 3:1. Karena lapisan perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ mengalami degradasi, sel yang dibuat mempunyai performansi rendah. Namun demikian, sel yang menggunakan perbandingan molar $\text{CH}_3\text{NH}_3\text{I}$ dan PbI_2 1:1 memberikan karakteristik listrik yang paling baik, dengan tegangan sirkit terbuka sebesar 0,04 V, densitas arus sirkit pendek sebesar 0,08 mA/cm², dan efisiensi konversi energi sebesar 0,002 %.

Kata Kunci: sel surya perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{I}$, PbI_2 , PCBM, PEDOT:PSS

I. INTRODUCTION

Nowadays hybrid halide perovskites enable outstanding photovoltaic performance due to their good electrical and optical properties. Hybrid perovskites are solids formed by an inorganic framework, usually a metal halide, intercalated by organic cations filling its voids, resulting in a polycrystalline material with octahedral arrangement. The formation of the crystals occurs spontaneously, driven by the self-assembly of the two precursors upon deposition [1]. One of the known perovskite material that is often used for the solar cells preparation is methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$).

Initially $\text{CH}_3\text{NH}_3\text{PbI}_3$ is utilized as sensitizers for liquid-state dye-sensitized solar cells in the form of nanoparticles which self-organized on the surface of a mesoporous TiO_2 films, replacing the dye in a liquid electrolyte-based device [2]. $\text{CH}_3\text{NH}_3\text{PbI}_3$ has a band gap of 1.55 eV, close to the optimum band gap for single junction which gives maximum efficiency (1.4 eV). This coupled with the good extinction coefficient (one order of magnitude higher than standard dyes, allows excellent external quantum efficiency spectra (EQE) until 800 nm, harvesting the photons in the visible range and part of the near-infrared of the solar spectra [3]. However, by this device structure the performance of these electrolyte-based perovskite solar cells degraded within only a few minutes due to the rapid decomposition of the hybrid halide perovskite in the redox electrolyte [4]. To solve this problem, Kim et al. developed solid-state perovskite-sensitized solar cells employing spiro-MeOTAD as the hole transport material (HTM), mesoscopic TiO_2 film as the electron transport material (ETM) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ as a sensitizer forming perovskite solar cells with a planar structure. By using this structure, it was obtained more stable cell with higher efficiency[5].

The use of mesoscopic TiO_2 as ETM requires high temperature processing, and as it has been known that the concentration and chemical composition of precursor solution strongly influence the thickness and microstructure of lead halide thin film and further more to the photovoltaic performance of the cells [6]. In order to be processed at low temperatures, here we report the fabrication of perovskite/polymer solar cells using $\text{CH}_3\text{NH}_3\text{PbI}_3$ as an absorber, PCBM (6,6 phenyl C61-butyric acid methyl ester) as an electron transport layer, and PEDOT/PSS as a hole transport layer. The device comprises a glass/ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Ag structure, where perovskite and polymers are deposited by spin coating. Spin-coating is a well-known, rapid technique used for producing uniform, quality thin films on a variety of substrates. This coating method is widely used in fabrication of organic electronics and optical device coatings, among many others [3]. In this research, we prepared a thin film of the low temperature solution-processed organometallic trihalide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) absorber by mixing $\text{CH}_3\text{NH}_3\text{I}$ (methyl ammonium iodide) with PbI_2 (lead iodide) in DMF (dimethyl formamide) solvent. The absorber, electron transport, and hole transport layers are deposited by spin coating of the solution. In order to obtain the optimum electrical characteristics, the mixture of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 are varied by the molar ratio of 1:1, 1:3, and 3:1, respectively.

II. EXPERIMENTAL SECTION

2.1 Materials

In this experiment we use materials as follow, indium tin oxide (ITO) coated glass substrates (Sigma Aldrich, 12 Ω/sq), HCl (Merck, 37%), $\text{CH}_3\text{NH}_3\text{I}$ (Sigma Aldrich), PbI_2 (Sigma Aldrich), DMF (Sigma Aldrich), PCBM (Sigma Aldrich), PEDOT:PSS (Sigma Aldrich), aerosol spray paint (PT Difan Prima Paint), paint thinner solution, acetone (Sigma Aldrich), isopropyl alcohol, and silver wire (Sigma Aldrich).

2.2 Instrumentation

All solution deposition processes are carried out on spinner coating equipment (Integrated Technologies, Inc.). Drying of deposited layers are carried out in vacuum oven (The Grieve Corporation). Digital hotplate/stirrer (Cimarec) is used to mix perovskite solution. Deposition silver metal is carried out in Auto 306 Vacuum Coater (Edwards). Ultraviolet spectrophotometer (Hewlett Packard 8453 Agilent Technologies) is used to measure the absorbance of perovskite layer. Solar simulator (Oriel Newport) is used as light source, and National Instrument source meter for measuring I-V characteristics.

2.3 Procedure

Fabrication of perovskite/polymer solar cells

In this work all chemicals are commercially available and used without further purification. The substrates used are indium tin oxide (ITO) coated glass in 12.5×12.5 mm dimensions with a sheet resistance of 12 Ω/sq. ITO is a transparent conductive oxide which serves to drain the generated hole. To avoid short circuit of the cell, it is necessary to form an ITO pattern by etching ITO partially. A black aerosol spray paint is sprayed on the ITO surface which has been patterned by adhesive tape mask previously. The substrates are then dried in room temperature overnight, and when they have dried, the masks are removed. The next step is etching process which aims to eliminate undesired ITO layer. Etching process is performed by dipping the substrates into 50% HCl solution for 5 minutes, followed by washing in DI water and dried. The remaining paint then removed by immersing the substrates into paint thinner solution, acetone, isopropyl alcohol, and DI water, respectively, for 10 minutes in ultrasonic bath.

The next step is coating of Poly(3,4-ethylene dioxy thiophene)-poly(styrene sulfonate) (PEDOT:PSS) which serves as a hole transport layer. PEDOT:PSS coating is carried out by spin coating method at a rotation speed of 1000 rpm for 60 seconds. The PEDOT:PSS layer is then dried in a vacuum oven at 120 °C for 60 minutes.

The organometallic halide perovskites are made by mixing CH₃NH₃I with PbI₂ in 1 mL DMF. The mixtures of CH₃NH₃I and PbI₂ are varied by the molar ratio of 1:1, 1:3, and 3:1, and stirred at room temperature for 24 hours. Subsequently, the mixtures are spin coated onto PEDOT:PSS layer at 2000 rpm for 30 seconds and annealed in a vacuum oven at 100 °C for 45 minutes.

The polymer solution is prepared by dissolving of 20 mg PCBM in 1 mL chlorobenzene and stirred for 60 seconds. The polymer layer is deposited onto perovskite layer by spin coating of the PCBM solution at 1000 rpm for 30 seconds, and then annealed in a vacuum oven at 100 °C for 10 minutes. Finally, a 60 nm-thick silver electrode is deposited by thermal evaporation onto the polymer layer at vacuum pressure of 5×10⁻⁵ mBar. The active area obtained of each cell is about 5.5×6 mm. The final structure of perovskite/polymer based solar cells is shown in Figure 1.

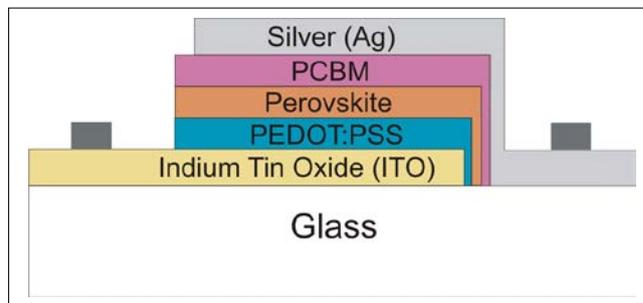


Figure 1. The structure of the fabricated perovskite/polymer solar cells

2.4 Characterization

The ultraviolet-visible absorption spectra of the CH₃NH₃PbI₃ layer are recorded by the ultraviolet spectrophotometer (Hewlett Packard 8453 Agilent Technologies). The photovoltaic performance of solar cells is measured with National Instrument source meter which is controlled by Lab-view software and using solar simulator (Oriel, Newport, USA, AM1.5) as a light source. The irradiation intensity is adjusted to 50 mW/cm² at 25 °C.

III. RESULTS AND DISCUSSION

3.1 Absorption Spectra of CH₃NH₃PbI₃

Figure 2 presents ultraviolet-visible absorption spectra of the CH₃NH₃PbI₃ layers resulted from the precursor solution of the mixed CH₃NH₃I and PbI₂ in the molar ratio of 1:1, 1:3, and 3:1, respectively. It can be seen that all perovskite layers exhibit a broad range of optical absorption with from 280 to 440 nm. According to the previous works [7], [8], the absorbance spectra of CH₃NH₃PbI₃ perovskite layer has a sharp

increase on the right edge of the curve at a wavelength (cut off wavelength) of about 780-800 nm. This wavelength is attributed to the band gap value of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite of about 1.55 eV. However, in this study the obtained absorbance spectra, has cut off wavelength in the range of about 440-540 nm (average = 480 nm). This wavelength value corresponding to the band gap of about 2.6 eV, which is the band gap of PbI_2 . Therefore, it can be ascertained that the perovskite layer formed mainly dominated by PbI_2 , and contains only a little of $\text{CH}_3\text{NH}_3\text{PbI}_3$. As a note that in this work, the preparation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer, from mixing $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 precursors until the deposition using a spin coating technique all performed in atmospheric environment without using a glove box. According to Niu et.al. [8], $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite will be decomposed back into $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 when exposed to humid air. They stated further that when $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer is exposed to humid air under sun light for 18 hours the cut off wavelength of the absorbance spectra will shift sharply from the origin, from the wavelength of 800 nm shifts to a wavelength of 540 nm, due to $\text{CH}_3\text{NH}_3\text{PbI}_3$ decomposed into $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 . The wavelength less than 520 nm corresponds to the PbI_2 band gap of about 2.6 eV [8].

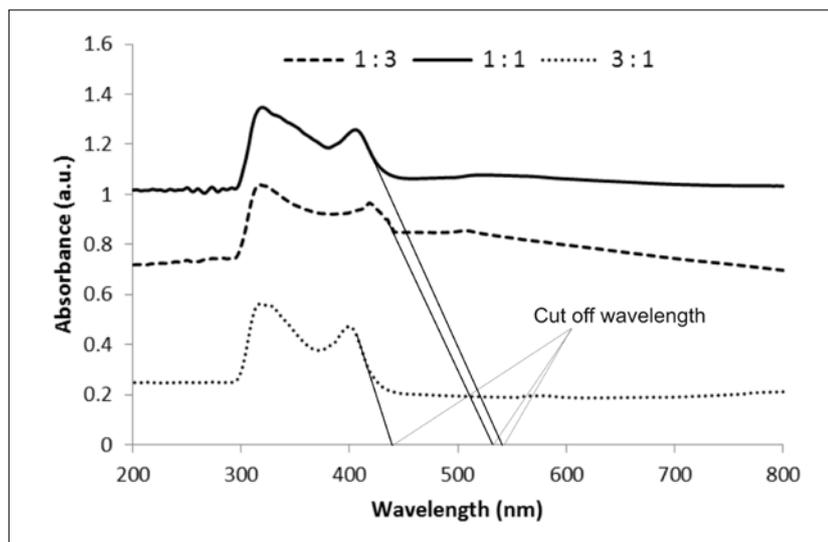


Figure 2. Ultraviolet-visible absorption spectra of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer resulted from the precursor solution of the mixed $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 in the molar ratio of 1:1, 1:3, and 3:1

Generally, there are two peaks between the wavelength ranges, first peak at shorter wavelength presumed for $\text{CH}_3\text{NH}_3\text{I}$, and second peak at longer wavelength for PbI_2 . The absorption peaks of each ratio are listed in Table-1. The first peak absorption of the molar ratio of 1:1 is located at 320 nm, and the second peak is located at ~405 nm. When the PbI_2 content increased, the first peak does not shift. However, the second peak shifts to blue region ~418 nm. If the PbI_2 content decreased, both of absorption peaks do not shift significantly. The highest absorption intensity is obtained by the 1:1 molar ratio. The intensity decreases with the increasing both of the $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 content. However, the increasing of PbI_2 amount significantly influences the absorption intensity of the layer and shifts the cut off wavelength of the absorption spectra to higher wavelength compared to that of $\text{CH}_3\text{NH}_3\text{I}$ amount. Higher cut off wavelength indicates that the layer contains more $\text{CH}_3\text{NH}_3\text{PbI}_3$.

3.2. Solar cells performance

The photovoltaic performance parameters of perovskite/polymer solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ are listed in Table 2. From the table, it is clear that the resulted values are very inferior if compared with the results of experiment which was carried out by Jeng et. al. [9]. By using same cell's configuration, they found greater values for all electrical characteristic parameters, where open-circuit voltage (V_{OC}), short circuit photocurrent (J_{SC}), and power conversion efficiency (PCE) are 0.60 V, 10.32 mA/cm^2 , and 3.9%, respectively. First possibility causing very low performance is the quality of the perovskite layer which is not dominated by $\text{CH}_3\text{NH}_3\text{PbI}_3$. As discussed before, the cells fabrication was not carried out under controlled

atmospheric conditions but exposed in humid air, so there was degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer into $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 . Therefore, with high PbI_2 content, only a little portion of semiconductor with narrow band gap which can absorb light to produce significant current. Second possibility is thickness of perovskite layer which is allegedly greater than 100 nm, electron-hole (charge carriers) diffusion length of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ [10]. In the thick perovskite layer, the generated charge carriers can recombine again before the carriers can reach to the respective electrode contact, resulting in the low current. Another possibility is non-uniform and uneven layers in the planar structure cell. This case can result in interpenetrating layers, so energy level of each layer involved in the cell is disturbed, causing the low V_{OC} .

Table 1. Absorption peaks and the absorbance of of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer resulted from the precursor solution of the mixed $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 in molar ratio of 1:1, 1:3, and 3:1.

CH ₃ NH ₃ I : PbI ₂ Molar Ratio	Absorption Peaks (nm)		Absorbance(a.u.)	
	First	Second	First Peak	Second Peak
1:3	317	418	1.0385	0.957
1:1	320	405	1.346	1.258
3:1	318	400	0.562	0.472

However, in general, Table 2 reveals that molar ratio of 1:1 gave higher performance than the others, with V_{OC} , J_{SC} , and PCE are 0.04 V, 0.08 mA/cm², and 0.002%, respectively, due to higher optical absorption and has greater $\text{CH}_3\text{NH}_3\text{PbI}_3$ content as discussed before. So the perovskite layer with molar ratio of 1:1 has better ability than 1:3 and 3:1 to absorb photons and convert it into current. The high $\text{CH}_3\text{NH}_3\text{I}$ content significantly contributed on the decrease of the J_{SC} and the V_{OC} . While with the higher PbI_2 content, the J_{SC} and V_{OC} are not changed.

Table 2. Electrical characteristic of $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells under 50 mW/cm² irradiation

CH ₃ NH ₃ I : PbI ₂ Molar Ratio	V_{OC} (Volt)	J_{SC} (mA/cm ²)	Efficiency (%)
1 : 1	0.039	0.085	0.0020
1 : 3	0.039	0.083	0.0012
3 : 1	0.019	0.024	0.0010

IV. CONCLUSION

We prepared a simple solution processed perovskite/polymer solar cell using $\text{CH}_3\text{NH}_3\text{PbI}_3$, PEDOT:PSS and PCBM as an absorber, an hole transport layer and an electron transport layer, respectively. The absorber solution was prepared by mixing in varied ratio of $\text{CH}_3\text{NH}_3\text{I}$ with PbI_2 in DMF solvent. Because of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer degraded into $\text{CH}_3\text{NH}_3\text{I}$ with PbI_2 , the fabricated cells have low performance. However, the cell using a ratio of 1:1 $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 gave the best electrical characteristics, resulted in an open circuit voltage of 0.04 V, a short circuit current density of 0.08 mA/cm², and a power conversion efficiency of 0.002 %.

ACKNOWLEDGEMENTS

This work was supported by Research Center for Electronics and Telecommunication Indonesian Institute of Sciences (PPET LIPI) through DIPA Tematik Programme 2016.

REFERENCES

- [1] S. Masi *et al.*, "Growing perovskite into polymers for easy-processable optoelectronic devices," vol. 5, p. 7725, Jan. 2015.
- [2] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal Halide Perovskites as Visible-Light

- Sensitizers for Photovoltaic Cells,” *J. Am. Chem. Soc.*, vol. 131, no. 17, pp. 6050–6051, May 2009.
- [3] P. P. Boix, K. Nonomura, N. Mathews, and S. G. Mhaisalkar, “Current progress and future perspectives for organic/inorganic perovskite solar cells,” *Biochem. Pharmacol.*, vol. 17, no. 1, pp. 16–23, 2014.
- [4] J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park, and N.-G. Park, “6.5% efficient perovskite quantum-dot-sensitized solar cell,” *Nanoscale*, vol. 3, no. 10, p. 4088, Oct. 2011.
- [5] H.-S. Kim *et al.*, “Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%,” *Sci. Rep.*, vol. 2, p. 591, 2012.
- [6] M. Wang, C. Shi, J. Zhang, N. Wu, and C. Ying, “Influence of PbCl₂ content in PbI₂ solution of DMF on the absorption, crystal phase, morphology of lead halide thin films and photovoltaic performance in planar perovskite solar cells,” *J. Solid State Chem.*, vol. 231, pp. 20–24, 2015.
- [7] R. Wu *et al.*, “Efficient electron-blocking layer-free planar heterojunction perovskite solar cells with a high open-circuit voltage,” *Org. Electron.*, vol. 26, pp. 265–272, 2015.
- [8] G. Niu, W. Li, F. Meng, L. Wang, H. Dong, and Y. Qiu, “Study on the stability of CH₃NH₃PbI₃ films and the effect of post-modification by aluminum oxide in all-solid-state hybrid solar cells,” *J. Mater. Chem. A*, vol. 2, no. 3, pp. 705–710, 2014.
- [9] J.-Y. Jeng *et al.*, “CH₃NH₃PbI₃ Perovskite/Fullerene Planar-Heterojunction Hybrid Solar Cells,” *Adv. Mater.*, vol. 25, no. 27, pp. 3727–3732, Jul. 2013.
- [10] G. Xing *et al.*, “Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH₃NH₃PbI₃,” *Science (80-.)*, vol. 342, no. 6156, pp. 344–347, Oct. 2013.