

Utilization of reuse PbI_2 for perovskite solar cell fabrication

J Yakiangngam¹, P Ruankham^{2,3}, S Choopun^{2,3} and A Intaniwet^{1,*}

¹School of Renewable Energy, Maejo University, Chiang Mai 50290, Thailand

²Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

³Thailand Center of Excellence in Physics (ThEP center), Commission on Higher Education, Bangkok 10400, Thailand

*Corresponding Author's E-mail: a.intaniwet@hotmail.co.th

Abstract. Perovskite solar cells have several advantages over traditional solar cells such as the ability to control the film morphology during the deposition and crystallization of the perovskite layer. The efficiency of perovskite solar cells can be modified using physical and chemical techniques to achieve better efficiencies. In this paper, we study the fabrication of typical inverted structure perovskite solar cell using reuse PbI_2 . The optimization condition of PbI_2 recycle based perovskite solar cell is reported with the maximum power conversion efficiency of 4.14% which is comparable to the cell made by fresh PbI_2 . Our finding has shown the potential of reuse PbI_2 precursor which eventually leads to cost reduction in perovskite solar cell fabrication.

Keywords: perovskite solar cells, reuse PbI_2 , inverted structure

1. Introduction

Perovskite solar cells have become commercially attractive with the potential of achieving large area with good flexibility, high efficiency and low production cost. These unique properties make perovskite solar cells the fastest-developing solar technology to date ^[1]. Their conversion efficiency has been dramatically increased from 3.8% in 2009 ^[2] to 22.7% in late 2017 ^[3]. Recently, a new approach for forming the PbI_2 nanostructure and the use of high $\text{CH}_3\text{NH}_3\text{I}$ concentration have been adopted to form a high quality perovskite film with better photovoltaic performances ^[4]. Self-assembled porous PbI_2 is formed by incorporating a small amount of additives into the PbI_2 precursor solutions, which significantly facilitate the conversion of perovskite without any PbI_2 residue. On the other hand, through employing a relatively high $\text{CH}_3\text{NH}_3\text{I}$ concentration, a highly crystallized and uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is achieved ^[5].

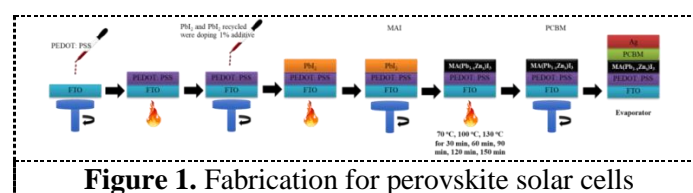
In almost every fabrication technique, PbI_2 is the main chemical substance that is employed in perovskite solar cell construction and is one of the major costs of perovskite solar cell. In this work, we explore the possibility of reusing PbI_2 for perovskite solar cell fabrication. The inverted structure of FTO/PEDOT: PSS/MA ($\text{Pb}_{1-x}\text{Zn}_x$) I_3 /PCBM/Ag perovskite solar cell is used in this study.

2. Methods

Perovskite solar cell fabrications were prepared with the detail describe as follows. 460 mg of each fresh PbI_2 (Sigma-Aldrich) and reuse PbI_2 was dissolved in 1 ml DMF solution (Sigma-Aldrich). The solution was stirred overnight at 70 °C. Zinc iodide additive was prepared by mixing 319 mg of Zinc iodide (Sigma-Aldrich) in 1 ml of DMF solution at 70 °C and it was stirred overnight using the magnetic stirrer. After that, 1% of Zinc iodide solution was added in the PbI_2 solution and the mixture was stirred overnight at 70 °C using the magnetic stirrer. 50 mg of MAI ($\text{CH}_3\text{NH}_3\text{I}$, Dyesol) was dissolved in 1 ml of 2-propanol solution (Sigma-Aldrich) at room temperature. 30 mg of PCBM (Ossila)

was dissolved in 1 ml of Chlorobenzene, (Sigma-Aldrich) at 70 °C to obtain PCBM solution. A fluorine-doped tin oxide (FTO) coated glass substrate was cleaned in an ultrasonic bath with detergent, deionized water, acetone and isopropanol, respectively. The substrate was then dried using the nitrogen and UV-ozone treatment for 30 min. PEDOT: PSS was later deposited onto the FTO substrate using the spin coating technique at 3000 rpm for 30 s and then the sample was annealed on the hotplate at 150 °C for 15 min in the ambient atmosphere to eliminate solvent residue. After that, the sample was directly taken into nitrogen filled glove box where the PbI_2 solution acquired as described above was spun on top of the PEDOT: PSS layer at 3000 rpm for 30 s. The PbI_2 layer was treated at 70 °C for 15 min on the hotplate. Subsequently, the MAI solution was spun at 2000 rpm for 30 s on top of the dried PbI_2 layer. The sample was then annealed on the hotplate at 70 °C, 100 °C and 130 °C for 30, 60, 90, 120, and 150 min. The PCBM solution was successively deposited on top of the MAI layer using the spin coater at 2000 rpm for 30 s. At the end, Ag metal was thermally evaporated on the PCBM layer to create the counter electrode for perovskite solar cell. Figure 1 summarizes the production process of the device used in this experiment.

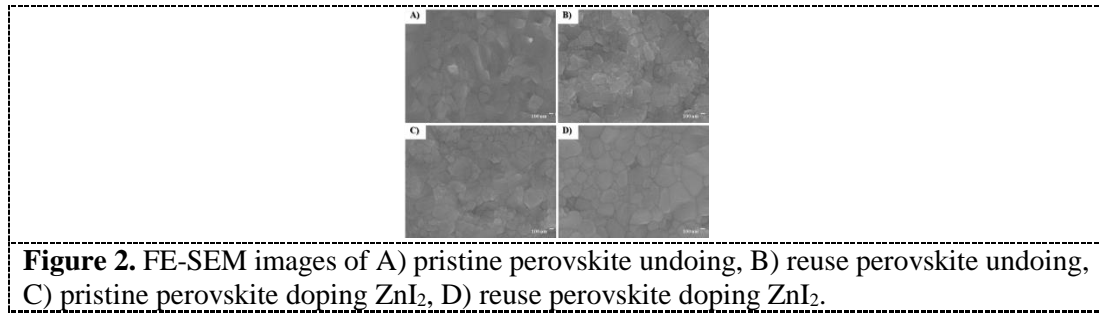
The performance of the solar cell was examined through the current density-voltage characteristics. The current and voltage of the device was measured using a voltage source-meter while being illuminated by the solar radiation at the intensity of 100 mWcm^{-2} using San-Ei Electric XES 301S solar simulator. The morphology of the perovskite film was studied using a field emission scanning electron microscope. The XRD spectra were obtained to confirm perovskite film formation using the X-ray diffraction technique.



3. Result and discussion

In this work, the used PbI_2 which was left over from the perovskite solar cell manufacturing process was gathered in the same container. It was gradually precipitated and was clearly seen at the bottom of the bottle. The mixture was then treated at 100 °C in order to evaporate solvents using a hotplate and the dried PbI_2 powder was used for the perovskite solar cell fabrication process.

Figure 2A-D shows the top-view FE-SEM images of the perovskite film surface. It was found that the addition of ZnI_2 during the fabrication of both pristine and reuse PbI_2 layers improves the film morphology. Good crystallinity of the perovskite film with a reasonably uniform grain size is clearly observed in the doped samples. The increase in crystal size confirms that ZnI_2 additive in the both PbI_2 precursors has exerted a crucial impact on the subsequent crystal growth processes. In order to provide a confirmation of the formation of perovskite film for various pristine and reuse PbI_2 samples, X-ray Diffraction (XRD) analysis has been employed in the study. The results are shown in Figure 2. For the annealing time between 30-150 min. The XRD patterns have demonstrated that a good crystalline nature with the (110) plane as the preferential orientation exists in the perovskite film. It is clearly seen that the perovskite samples treated at 120 min offer the highest (110) peak for both pristine and reused PbI_2 . The (220) peak is also visible with lower intensity compared to that of (110) and, similar to (110), the samples annealed at 120 min show the highest peak. The annealing time obviously has some influence on the completion of perovskite films. Longer annealing time results in better completion of perovskite. But when compared between pristine PbI_2 and reuse PbI_2 , the peak at (110) of the sample fabricated using pristine PbI_2 is higher than that using reuse PbI_2 . At the annealing time of 30 min, the conversion of perovskite is not complete and the peak at 12.6° is weakly visible which indicates the existence of PbI_2 .



The photovoltaic performances of the devices are investigated using the J-V curve measurement. The perovskite solar cells are fabricated using pristine and reuse PbI₂ with 1% of ZnI₂ additive in the perovskite layer. Figure 4A shows different J-V curves of perovskite solar cells that were fabricated using pristine PbI₂ for different annealing times. It can be seen that lower annealing time provides poor photovoltaic performance while higher annealing time (with duration of >120 min) offers a reasonable well performance. Similarly, the cell fabricated using reuse PbI₂ shows relatively better performance when annealed at a higher time (Figure 4B). The comparison of photovoltaic performance of the device fabricated using pristine and reuse PbI₂ can be displayed in Figure 5. The J-V curve for both devices shows a similar trend and this implies that it is possible to use reuses PbI₂ for perovskite production.

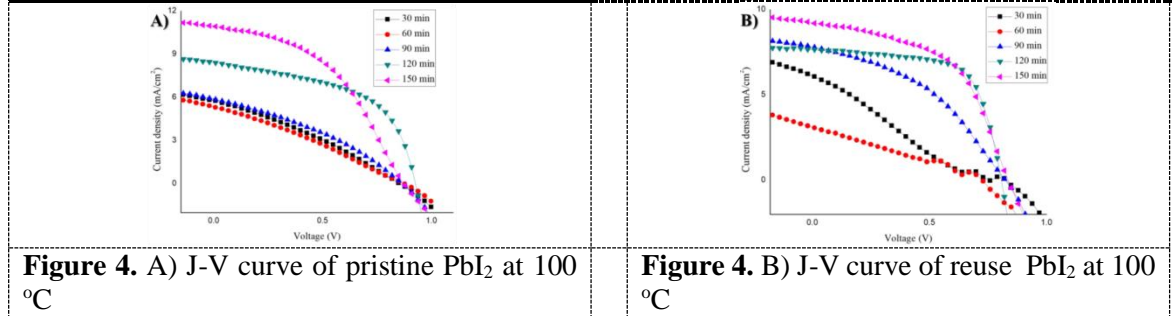
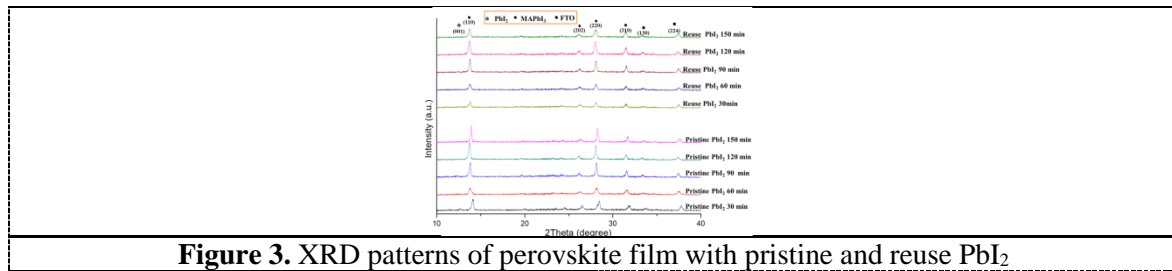


Table 1 summarizes the photovoltaic performance parameters for every cells tested in this work. The undope PbI₂ devices (both pristine and reuse) show a relatively low energy conversion efficiency due to low quality of film morphology as seen in Figure 2. A small addition of ZnI₂ improves the film morphology and the pristine PbI₂ perovskite solar cell exhibits the highest conversion efficiency of 4.33% with the fill factor of 0.46 when annealed for 150 min. The best fill factor (FF), however, occurs when the device is treated for 120 min with the conversion efficiency of 4.18%. The results correlate well with the XRD results where the completion of perovskite conversion occurs at the annealing temperature greater than 120 min. The perovskite solar cell fabricated using PbI₂ reuse shows the maximum conversion efficiency of 4.14% with the fill factor of 0.68 at the annealing time of 120 min. The J_{sc} and V_{oc} values are also relatively lower compared to those from pristine PbI₂ devices. From the XRD results (Figure 3), the cells made by pristine PbI₂ shows higher intensity of (110) peak compared to that of reuse PbI₂ implying better perovskite conversion and hence a slightly high energy conversion efficiency of the device.

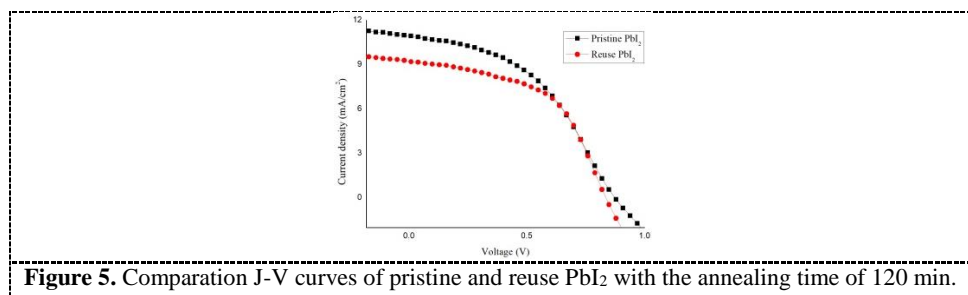


Figure 5. Comparison J-V curves of pristine and reuse PbI₂ with the annealing time of 120 min.

Table 1 Photovoltaic parameters of pristine and recycle PbI₂

Samples	Annealing temp (°C)	Annealing time (min)	Jsc (mA/cm ²)	Voc (V)	FF	PCE (%)
pristine PbI ₂ (undope)	100	120	6.53	0.91	0.38	2.78±0.04
pristine PbI ₂ (doped)	100	30	5.82	0.85	0.31	1.45±0.04
		60	5.42	0.88	0.29	1.34±0.04
		90	5.94	0.85	0.35	1.75±0.04
		120	8.47	0.91	0.54	4.18±0.04
		150	10.9	0.85	0.46	4.33±0.04
reuse PbI ₂ (undope)	100	120	6.45	0.82	0.44	2.63±0.04
reuse PbI ₂ (doped)	100	30	6.23	0.73	0.24	1.05±0.04
		60	3.19	0.70	0.28	0.52±0.04
		90	7.87	0.82	0.41	2.14±0.04
		120	7.68	0.79	0.68	4.14±0.04
		150	9.29	0.82	0.54	4.09±0.04

4. Conclusion

In conclusion, we investigate the possibility of reuse PbI₂ in perovskite solar cell fabrication. The film morphology is greatly improved upon the addition of small amount of ZnI₂. The results show that the highest photovoltaic efficiency of pristine and reuse PbI₂ are 4.33% and 4.14%, respectively. Appropriate annealing temperature of perovskite film at 100 °C and annealing time longer than 120 min provides the best condition for perovskite formation. Reuse PbI₂ can be used to fabricate the perovskite solar cell and reuse of PbI₂ will lead to lower the environmental pollution due to toxicity of Pb and will reduce the cost of perovskite solar cells in the future.

5. Acknowledgement

J Yakiangngam would like to acknowledge a scholarship from School of Renewable Energy, Maejo University. The authors greatly appreciate the financial support from the Energy Policy and Planning Office, Ministry of Energy, Thailand. The financial support from Department of Physics and Materials Science, Faculty of Science, Chiang Mai University and Thailand Centre of Excellence in Physics (ThEP centre), is greatly acknowledged.

References

- [1] Joseph M S, Chistians S, et al. 2016 Intriguing Optoelectronic Properties of Metal Halide Perovskite, *Chem. Rev.* **116** (21) 12956.
- [2] Teshima K A, Shirai K, et al. 2009 Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **131** (17) 6050.
- [3] Song J, Yang Y, et al. 2017 Morphology modification of perovskite film by a simple post-treatment process in perovskite solar cell. *Mate and Engin. B* **217** 18.
- [4] Zhao W, Yang D, et al. 2017 Zn-doping for reduced hysteresis and improved performance of Methylammonium lead iodide perovskite hybrid solar cells. *Mate. Tod. Energ.* **5** 205.
- [5] Mohammadian N, Alizadeh A H, et al. 2016 A two-step spin-spray deposition processing route for production of halide perovskite solar cell. *Thin. Solid. Films.* **616** 754.