

PAPER • OPEN ACCESS

## Improved Solar Cell and Photoresponse Performance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite with ZnO Nanorods

To cite this article: Anggun A Fibriyanti *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **515** 012089

View the [article online](#) for updates and enhancements.

# Improved Solar Cell and Photoresponse Performance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite with ZnO Nanorods

Anggun A Fibriyanti<sup>1</sup>, Nandang Mufti<sup>1,2\*</sup>, Abdulloh Fuad<sup>1,2</sup>, Eny Latifah<sup>1</sup>, Robi Kurniawan<sup>1</sup>, Chusnana I Yogihati<sup>1</sup>, Nurul Hidayat<sup>1,2</sup>

<sup>1</sup> Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia

<sup>2</sup> Centre of Advanced Materials for Renewable Energy (CAMRY), Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia

\*Corresponding author's email: [nandang.mufti.fmipa@um.ac.id](mailto:nandang.mufti.fmipa@um.ac.id)

**Abstract:** The  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite has great interest due to good candidate for low cost solar cell and photodetector. The research of this report is to investigate the effect of growth time to the morphology of ZnO NRs and its performance of solar cell and photoresponse. The ZnO NRs were grown at growth time of three and four hours on the ZnO seed layer using hydrothermal method. While perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  were synthesized by one-step spin coating. The  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs samples was characterized by x-ray diffraction for structural properties analysis and scanning electron microscopy for morphological properties. The  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs samples performance was measured by solar simulator under light illumination. The XRD results show that PSC has ZnO and  $\text{CH}_3\text{NH}_3\text{PbI}_3$  phases with small impurities of  $\text{PbI}_2$ . The growth time increases the length of ZnO NRs and in combination with  $\text{CH}_3\text{NH}_3\text{PbI}_3$  can enhance performance of solar cell and photoresponse.

**Keywords:** Solar cell,  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , perovskite, ZnO, nanorod, photoresponse performance

## 1. Introduction

Perovskite is one of the new photovoltaic materials for renewable solar energy [1], due to among the abundant perovskite materials with structural form of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  have a band gap of 1.5 eV and excellent light absorbing characteristic, low exciton-binding energy, fast photogeneration, excellent charge carrier mobility, and long electron-hole diffusion [2]. The structural of perovskite solar cells (PSC) consists of Electron Transport Layer (ETL), Light Absorption, and Hole Transport Layer (HTL). Each layer plays an essential role in enhancing the PSC performance, such as efficiency and stability. Nowadays, the power conversion efficiencies of PSC can achieve up to 23% [3]. However, the instability of PSC remains a challenge for application [4]. Perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  ions are easy to degrade in a humid environment [5]. Various efforts have been studied to solve this problem, for example by modifying the ETL structure layer.

Among several materials, which are applied as ETL, zinc oxide (ZnO) received great attention due to it has a large band gap of ~3.3 eV with large excitation binding energy 60 meV and high electron mobility. ZnO in the form of nanorod is more effective in collecting charges due to larger surface area



[6]. Several methods based on chemical synthesis of ZnO NRs have been reported, for example, pyrolysis [7], sol-gel [8], and hydrothermal with one step or two step method [9,10].

Several works have successfully synthesized  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite as photodetectors [11]. organolead halide perovskite shows photoresponsivity 22 and  $12 \text{ AW}^{-1}$  by shining 405 nm and 532 nm lasers [12]. More effort has been made to increase photosensitivity in broadband spectra, such as the introduction of a bipolar  $\text{MoO}_3$  interface layer between electrode perovskite and the electrode can increase photoresponse speed with rising time and decay time of 21.6 and 9.9 ms, respectively [11]. Ultrahigh responsivities with low-voltage high-gain based on perovskite in a broadband region from the ultraviolet to the near infrared have been reported by Xie *et al.* [13]. However, photodetectors with low-cost and facile solution process remains a challenge.

In this study, we report the effect of ZnO NRs morphology in combination with  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite to the performance of solar cell and photoresponse. The different morphology of ZnO NRs produced from the variation of growth time at four and three hours. ZnO NRs synthesized using a two-step hydrothermal method whereas  $\text{CH}_3\text{NH}_3\text{PbI}_3$  coated by one step spin coating. We use the  $\text{Cu}_2\text{O}$  layer as hole transport material synthesized by chemical bath deposition.

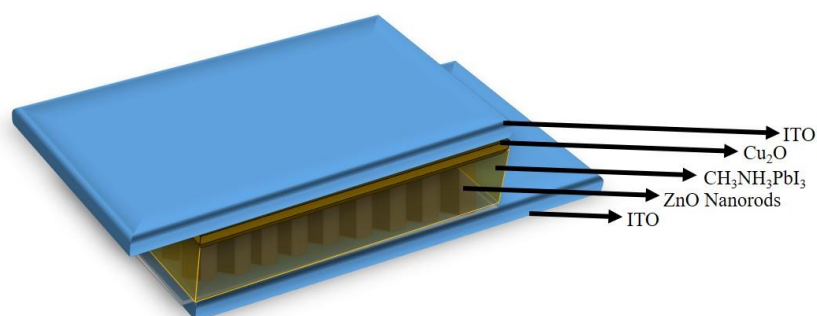
## 2. Methods

ZnO NRs were synthesized by the hydrothermal method. ZnO nanorods were grown on ZnO seed layer on ITO glass. The ITO glass was cleaned using acetone, and deionized water in the ultrasonic cleaner for 15 min. The ZnO seed layer was coated by spin coating with a sol-gel solution, containing zinc acetate dihydrate, ethanol, and monoethanolamine. Zinc nitrate tetrahydrate was dissolved by deionized water using magnetic stirrer at room temperature for 25 min for ZnO NRs precursor solution. Furthermore, the coated ZnO films were dipped in ZnO NRs solution at temperature  $90^\circ\text{C}$  with growth time variation at 4 and 3 hours using the hydrothermal method. Then the samples were annealed at  $400^\circ\text{C}$  for 15 minutes.

$\text{CH}_3\text{NH}_3\text{PbI}_3$  layer was fabricated using a one-step spin coating method. Firstly, The  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solution precursor consists of methylammonium iodide ( $\text{CH}_3\text{NH}_3\text{I}$ ), and the  $\text{PbI}_2$  powder was mixed with dimethyl sulfoxide (DMSO) solution and N, N-dimethylformamide (DMF). Then, the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solution was coated on the ZnO NRs layer by spin coating for 20 s at 3000 rpm. Then, the anti-solvent diethyl ether was dropped on to the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film. The sample of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film was preheated with the face-up position for 1 min at a temperature of  $40^\circ\text{C}$  and annealed with face-down position at a temperature of  $100^\circ\text{C}$  for 10 min.

$\text{Cu}_2\text{O}$  layers as a Hole Transport Layer (HTL) was prepared by using chemical bath deposition. NaOH was diluted by aquadest at a temperature  $70^\circ\text{C}$  as A solution. Then,  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_2\text{O}_3$  dissolved in aquadest as B solution. Then A and B solutions were mixed. The ITO substrate was immersed in to mix solutions to form a yellow  $\text{Cu}_2\text{O}$  layer.

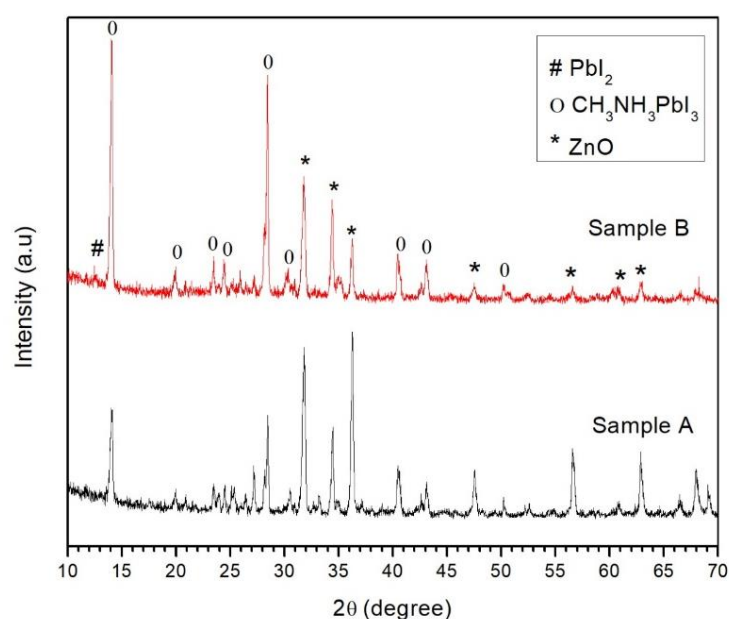
PSC devices are formed like the schematic as shown in Figure 1 where the layer structure consists layers of ITO/ZnO Nanorods/ $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{Cu}_2\text{O}$ /ITO film. PSC device was characterized with X'Pert Pro Panalytical XRD for structural properties and SEM (Merk FEI, Type: Inspect-S50) for surface morphology. Solar cell performance measured by solar simulator under  $20 \text{ mW/cm}^2$  illumination. Whereas, the photoresponse performance measured by electrometer Keithley 6517A.



**Figure 1.** Schematic Illustration of PSC device

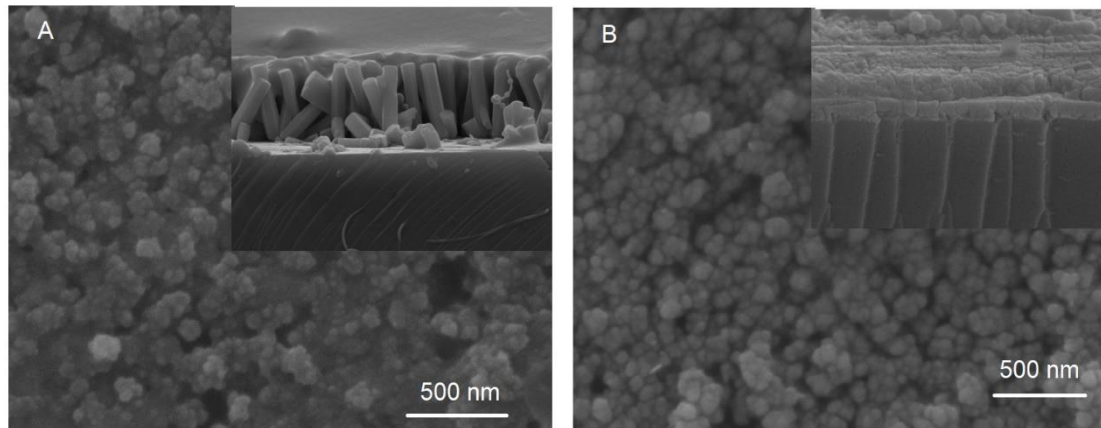
### 3. Results and Discussion

The diffraction pattern of the  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs shown in Figure 1 where sample A and sample B are  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs with growth time of 4 and 3 hours, respectively. The XRD pattern analyzed by comparing with crystallography open database (COD) with ID 7218931 for  $\text{CH}_3\text{NH}_3\text{PbI}_3$  phase and American Mineralogist Crystal Structure Database (AMCSD) with ID 0011819 for  $\text{PbI}_2$  phase and ID 0005203 for ZnO phase. The XRD result shows that the diffraction pattern of sample A and B consists of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ ,  $\text{PbI}_2$ , and ZnO nanorods phases. The Phase of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  appears at  $2\theta$   $14.37^\circ$ ,  $19.97^\circ$ ,  $23.46^\circ$ ,  $24.62^\circ$ ,  $28.36^\circ$ ,  $30.22^\circ$ ,  $40.47^\circ$ ,  $43.03^\circ$  can be indexed to (110), (112), (211), (202), (004), (220), (213), and (224) planes, respectively. While, the angles at  $31.84^\circ$ ,  $34.41^\circ$ ,  $36.51^\circ$ ,  $47.23^\circ$ ,  $56.54^\circ$ ,  $60.73^\circ$  can be identified as ZnO phase. The  $2\theta$  of  $12.41^\circ$  related with  $\text{PbI}_2$  phase. The diffraction pattern of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite is in accordance with previous results reported by Yu *et al.* [12]. The original compound of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite is tetragonal crystal structure and space group of  $I4/mcm$ . The highest peak of ZnO NRs in Sample A is (101) plane with  $2\theta$  of  $36.51^\circ$ . While for sample B is (100) plane at  $2\theta$   $31.84^\circ$ . This phenomenon indicates that the growth time ZnO NRs affect the crystal orientation.



**Figure 1.** XRD pattern of the ITO/ZnO NRs/  $\text{CH}_3\text{NH}_3\text{PbI}_3$  with different growth time

Figure 2 shows the SEM image of  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs for Sample A and Sample B. The distribution and diameter size of Sample A and B are similar. In contrast, the cross-sectional of the SEM image in the inset of Figure 2 shows the different length of ZnO NRs. The ZnO NRs at the growth time of 4 hours has length rod around  $500\text{ }\mu\text{m}$ . While for a growth time of 3 hours seems not growing well. The growth time effects to the length rather than the diameter of ZnO NRs which is similar with the previous result reported by Pacholski *et al.* [15]. Therefore, the growth time of ZnO NRs should be longer than 3 hours in order to grow well.

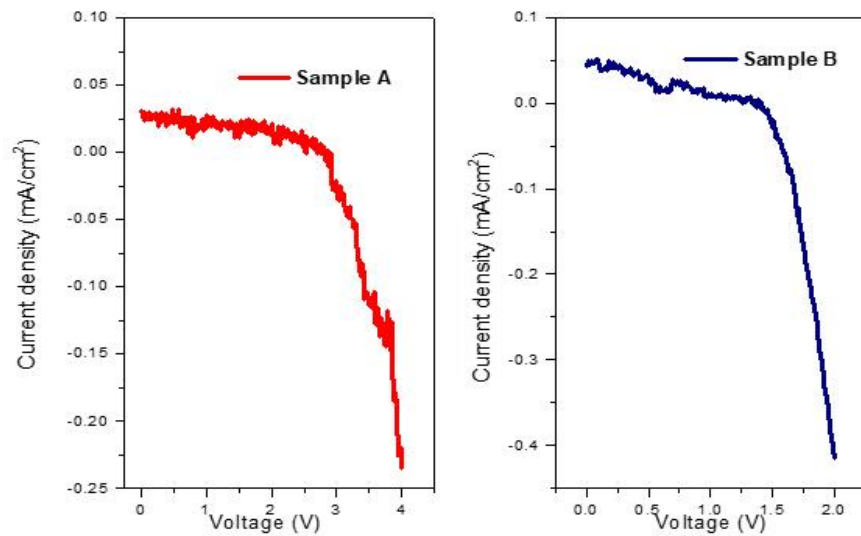


**Figure 2.** Morphology of the  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs with different growth time (a) 4 hours, (b) 3 hours. The inset is the cross section of ZnO NRs.

The current graph density versus voltage (J-V) of  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs obtained from solar simulator measurement shown in Figure 3. Based on this graph then can be obtained the solar cell parameters performance as summarized in Table 1. Sample A with growth time of 4 hour has a power cell efficiency of 0.41% higher than sample B with growth time of 3 hour due to longer rods have better in light absorption light [14].

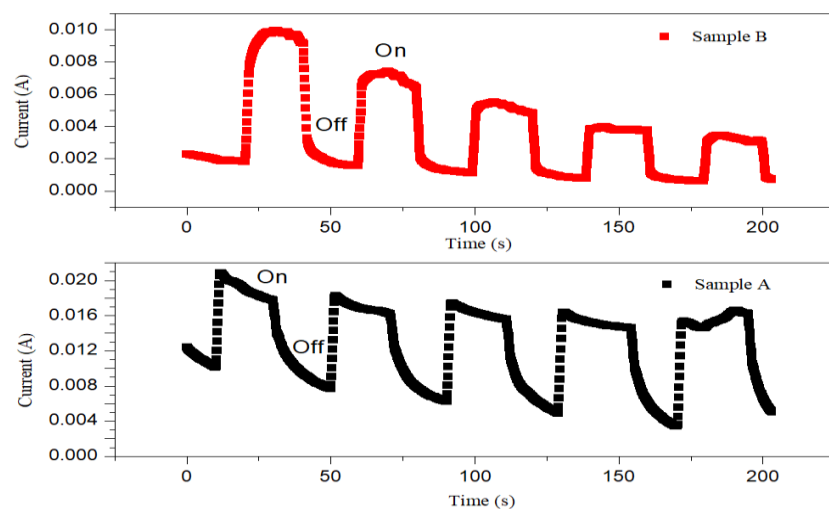
**Table 1.** Performance parameters of the ZnO nanorods based on  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cells

Parameter	Sample A	Sample B
$I_{sc}$ (mA)	0.05	0.07
$J_{sc}$ (mA/cm <sup>2</sup> )	0.03	0.04
$V_{oc}$ (V)	2.89	1.26
Fill Factor (%)	0.49	0.36
$P_{max}$ (mW)	0.07	0.03
$I_{max}$ (mA)	0.03	0.04
$V_{max}$ (V)	1.88	0.81
$R_s$ (ohm)	1492	2388
PCE (%)	0.41	0.19



**Figure 3.** Graph of current density ( $J$ ) as function of voltage ( $V$ ) of  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs for sample A ( growth time of 4 hours) and sample B (growth time of 3 hours)

In general, the performance of photoresponse of  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$  NRs measured by electrometer Keithley 6517A under on/off light illumination cycle as shown in Figure 4. The current change in sample A is around 10 mA and stable up to the fifth cycle. While the current change in sample B is 8 mA for the first cycle and decrease to 3 mA after the fifth cycle. This result indicates that the long rods of ZnO play an important role in photoresponse performance. Moreover, time rise of both sample is short and similar, whereas time decay of sample A is longer than sample B. Time rise of both samples is shorter due to the illumination of light in ZnO NRs produces electron-hole pairs [ $h\nu \rightarrow e^- + h^+$ ]. Therefore, excitation electrons from the conduction band to valence band are more efficiently. at the same time, the hole will oxidize the oxygen ions on the surface [ $\text{O}_2^- + h^+ \rightarrow \text{O}_2$ ]. When the light turns off, the releasing hole in long Rod that reacted with oxygen ions is more difficult due to the oxidation process is also take times to oxidize [22]. Consequently, times decay in long rods of sample A is higher than sample B.



**Figure 4.** Photoresponse of the device ZnO nanorods based on  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cells

#### 4. Conclusion

The growth time affects the length rather than the diameter of ZnO NRs. The length of ZnO NRs with growth time of 4 hours is around 500 nm. The structure of the perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  layer has been synthesized successfully with tetragonal crystal structure and space group of  $I4/mcm$ . The best power efficiency cell of ZnO NRs/  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is 0.4%. The ZnO NRs/  $\text{CH}_3\text{NH}_3\text{PbI}_3$  with the longer rod has stable photoresponse. The ZnO NRs with long rods improves both the solar cell and photoresponse performance.

#### References

- [1] Huang J, Yuan Y, Shao Y and Yan Y 2017 Understanding the physical properties of hybrid perovskites for photovoltaic applications
- [2] Niu G, Guo X and Wang L 2015 Review of recent progress in chemical stability of perovskite solar cells *Journal of Materials Chemistry A* **3** 8970–80
- [3] Zhang P, Wu J, Zhang T, Wang Y, Liu D, Chen H, Ji L, Liu C, Ahmad W, Chen Z D and Li S 2018 Perovskite Solar Cells with ZnO Electron-Transporting Materials *Advanced Materials* **30**
- [4] Shaikh J S, Shaikh N S, Sheikh A D, Mali S S, Kale A J, Kanjanaboos P, Hong C K, Kim J H and Patil P S 2017 Perovskite solar cells: In pursuit of efficiency and stability *Materials & Design* **136** 54–80
- [5] Bu I Y Y and Yang C-C 2012 High-performance ZnO nanoflake moisture sensor *Superlattices and Microstructures* **51** 745–53
- [6] Son D-Y, Im J-H, Kim H-S and Park N-G 2014 11% Efficient Perovskite Solar Cell Based on ZnO Nanorods: An Effective Charge Collection System *The Journal of Physical Chemistry C* **118** 16567–73
- [7] Karami H and Fakoori E 2011 Synthesis and Characterization of ZnO Nanorods Based on a New Gel Pyrolysis Method *Journal of Nanomaterials*
- [8] M. Saleem, 2012 Effect of zinc acetate concentration on the structural and optical properties of ZnO thin films deposited by Sol-Gel method *International Journal of the Physical Sciences* **7**
- [9] Fuad A, Fibriyanti A A, Subakti, Mufti N and Taufiq A 2017 Effect of Precursor Concentration Ratio on The Crystal Structure, Morphology, and Band Gap of ZnO Nanorods *IOP Conference Series: Materials Science and Engineering* **202** 012074
- [10] Fuad A, Fibriyanti A A, Mufti N and Taufiq A Growth of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  Perovskite on Stainless Steel Substrate Layered by ZnO Nanoparticles Using One-Step Spin Coating Route **3** 1–6
- [11] Yu J, Chen X, Wang Y, Zhou H, Xue M, Xu Y, Li Z, Ye C, Zhang J, van Aken P A, Lund P D and Wang H 2016 A high-performance self-powered broadband photodetector based on a  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite/ZnO nanorod array heterostructure *J. Mater. Chem. C* **4** 7302–8
- [12] Liu J, Xue Y, Wang Z, Xu Z-Q, Zheng C, Weber B, Song J, Wang Y, Lu Y, Zhang Y and Bao Q 2016 Two-Dimensional  $\text{CH}_3\text{NH}_3\text{PbI}_3$  Perovskite: Synthesis and Optoelectronic Application *ACS Nano* **10** 3536–42
- [13] Xie C, You P, Liu Z, Li L and Yan F 2017 Ultrasensitive broadband phototransistors based on perovskite/organic-semiconductor vertical heterojunctions *Light: Science & Applications* **6** e17023
- [14] Li S, Zhang P, Wang Y, Sarvari H, Liu D, Wu J, Yang Y, Wang Z and Chen Z D 2017 Interface engineering of high efficiency perovskite solar cells based on ZnO nanorods using atomic layer deposition *Nano Research* **10** 1092–103
- [15] Pacholski C, Kornowski A and Weller H 2002 Self-assembly of ZnO: From nanodots to nanorods *Angewandte Chemie - International Edition* **41** 1188–91
- [16] Tseng Z-L, Chiang C-H and Wu C-G 2015 Surface Engineering of ZnO Thin Film for High Efficiency Planar Perovskite Solar Cells *Scientific Reports* **5** 13211

**Acknowledgments**

This research was supported by DRPM, Ministry of Research, Technology and Higher Education (Kemenristekdikti) of the Republic of Indonesia under PDUPT grant 2018.