

Role of polyethylene glycol addition on the improvement of P3HT:PCBM organic solar cells

Tetsuo Soga^{*}, Seiya Kato, Shinya Kato and Naoki Kishi

Department of Electrical and Mechanical Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466-8555

*** Corresponding author**

Email: soga@nitech.ac.jp, tel: +81-52-735-5532, fax: +81-52-735-7120

In this work, the power conversion efficiency (PCE) of bulk heterojunction organic solar cell is improved by adding PEG (polyethylene glycol) in the solution of P3HT and PCBM blend. The short circuit current and fill factor are increased by adding PEG with the molecular weight of 300, whereas the open circuit voltage is not changed. On the other hand, PCE becomes worse by adding PEG with the molecular weight of 6000. It was observed by field-emission scanning electron microscopy that the additional layer was formed under the active layer during spin coating by phase separation. The stability of solar cell is also improved with introducing the PEG layer. These results were explained by the formation of the PEG interfacial layer under the P3HT:PCBM active layer, which acts as a hole transport layer and also blocks the water diffusion from PEDOT:PSS toward the metal electrode.

Keywords: Organic solar cell, photovoltaic, P3HT, PCBM, polyethylene glycol, interfacial layer, phase separation

1. Introduction

Organic solar cells (OSCs) have attracted attentions since early times because of low manufacturing cost, low fabrication temperature and flexibility of organic materials. It is expected that the mass production of OSCs becomes possible by roll-to-roll process in the future [1]. Although the power conversion efficiency (PCE) was low (less than 1%) until the 1980s [2, 3], OSCs have emerged as a next generation solar cell after the bulk heterojunction was reported in 1990s [4-6]. The bulk heterojunction is a structure where a donor material and an acceptor material are blended in the active layer, and has become a standard structure to obtain high efficiency recently. In order to improve the PCE of bulk heterojunction solar cell, a lot of research has been done [7-9]. Recently, the PCE higher than 12% has been reported by using bulk heterojunction structure using novel organic materials [10-12]. It is predicted that more than 20 % can be possible by a single organic solar cell in the future [13].

In the case of organic solar cells using PCBM (6,6-Phenyl-C₆₁-Butyric Acid Methyl Ester) as an acceptor and P3HT (poly 3-hexylthiophene) as a donor, the blend of PCBM and P3HT is usually spin-coated on the PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate)) hole-transport layer formed on ITO (indium tin oxide) glass substrate, followed by the evaporation of electrode metal such as Al [14]. For the improvement of PCE, the buffer layer is inserted between PEDOT:PSS and the active layer or between the active layer and the metal electrode [15-18]. However, the fabrication process becomes complicated and the insertion of the buffer layer may cause the degradation of the underlying layer. Since the interface control is a key issue to improve the performance of device [13, 19, 20], the further investigation is necessary [21-23].

One simple way to make a buffer layer of organic solar cell is to use phase separation of organic materials. The spontaneous phase separation of P3HT and PEG (polyethylene glycol) was reported by Deckman et al. in 2014. It was reported that the ITO glass/PEDOT:PSS/PEG/P3HT structure is formed by the spontaneous phase separation when the P3HT:PEG blend solution is spin coated on ITO glass/PEDOT:PSS [24]. The improvement of PCBM:P3HT bulk heterojunction solar cell was also reported by using PEG as an additive [25]. By adding PEG into the blend of PCBM:P3HT solution, the open circuit voltage and the short circuit current were improved through spontaneous phase

separation of PEG. However, there is no systematic investigation of solar cell performance for different amount of PEG for different molecular weight. The mechanism of improved photovoltaic properties by using PEG has not been clarified yet.

This paper describes the improvement of P3HT:PCBM bulk heterojunction solar cell by adding PEG in the active layer during spin coating to form an interfacial layer. In this work, the evidence that the PEG interfacial layer is formed under the active layer is presented using cross-sectional field emission scanning electron microscope for the first time, and the photovoltaic properties of PCBM:P3HT bulk heterojunction organic solar cells by adding PEG in the active layer during the spin coating for different amount and for different molecular weight are investigated. Moreover, the PCBM:P3HT organic solar cell performance without PEG is compared with those with PEG layer formed on the active layer and under the active layer by spin coating separately. The stability of solar cell with PEG layer was compared with that without PEG interfacial layer.

2. Experimental methods

Regioregular P3HT (Merk) and PCBM (Nano Spectra) were used as donor material and acceptor material, respectively, without any purification. 15 mg P3HT, 15 mg PCBM and different amount of PEG (0, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 8.0 mg) with the molecular weight of 300 (PEG 300) and 6000 (PEG 6000) were dissolved in 1 mL 1,2-dichlorobenzene, and vigorously stirred in globe box. The two molecular weights were chosen since PEG 300 is expected to improve the solar cell performance and PEG 6000 is expected to degrade the solar cell performance from the literature [25]. The ITO glass substrates (sheet resistance is $10 \ \Omega/\square$) were sequentially cleaned in ultrasonic bath using acetone and ethanol. Water based PEDOT:PSS solution (Clevios) was spin coated on ITO glass at 4000 rpm for 20 s, followed by the spin coating of active layer at 1000 rpm for 50 s. After the solvent annealing was performed in dichlorobenzene for 1 hour at room temperature, the samples were annealed for 30 min at 70°C in glove box to improve the crystal quality of P3HT. For the solar cell characteristics measurement, an approximately 100-nm-thick Al electrode was thermally evaporated on the active layer. Then the samples were annealed for 10 min at 100 °C in the case of PEG 300 and at 140 °C in the case of

PEG 6000, which are the optimum annealing temperature, which will be reported elsewhere. The complete solar cell structure is shown in Fig. 1 (a).

In order to clarify the effect of PEG layer, the PEG layer was separately formed by spin coating using the PEG solution dissolved in ethanol. The solar cell structures shown in Fig. 1(b) and 1 (c) were fabricated and the photovoltaic properties were tested. In Fig. 1(b), the PEG layer is under the P3HT:PCBM active layer and the PEG layer is on the active layer in Fig. 1 (c). The area of active layer is 0.09 cm^2 . The solar cell was stored in dark under nitrogen atmosphere until measurement. The solar cells were characterized by field-emission scanning electron microscope (FE-SEM) system (JEOL, JXA-8530F) with the acceleration voltage of 10kV and ultraviolet visible light spectrophotometer (JASCO, V-570). The photovoltaic properties were measured under standard solar simulator irradiation of 100 mW/cm^2 (AM1.5) at room temperature.

3. Results and discussion

In order to examine the photo absorption by the PEG layer, the transmission spectra of the solar cell without Al electrode were measured. Fig. 2 is the typical transmission spectra of solar cells with and without PEG 300. The discontinuity at around 800 nm is due to the equipment used for the measurement. The amount of PEG is 2 mg. The drop of transmission in the wavelength range shorter than 650 nm is due to the absorption of P3HT and PCBM. Although there is small difference at around 500 nm to 600 nm, which may be due to PEG, the difference is not large enough to affect the solar cell performance. no much difference in the two spectra. Therefore, the effect of absorption by PEG on the solar cell performance is negligible.

Fig. 3 shows the J-V characteristics of solar cells with different amount of PEG 300, and the short circuit current density (J_{sc}), the open circuit voltage (V_{oc}), fill factor (FF) and PCE are shown in Fig. 4. The J_{sc} increases with increasing the amount of PEG and has a maximum at around 2 mg, then decreases. On the other hand, there is no much change in the V_{oc} for various PEG content. The FF slightly increases with increasing the PEG amount. Therefore PCE increases with PEG addition and has a maximum at 2 mg. From Fig. 4 it can be interpreted that the increase of the FF is due to the reduction of series resistance. No

change in the V_{oc} by PEG layer addition is due to that the V_{oc} is determined by the HOMO level of P3HT and the LUMO level of PCBM [26]. The improvement of FF would be due to the reduction of series resistance in solar cell by the doping of PEG in the organic layer. The decrease in the resistance of organic films by PEG doping is reported [27].

In order to clarify the reason why J_{sc} increases with PEG addition in P3HT:PCBM blend, the samples were characterized by cross-sectional FE-SEM. Fig. 5 shows the SEM images of P3HT:PCBM solar cell (a) without PEG, (b) with PEG 300 (2mg) and with PEG 300 (8mg). When PEG is not added, only Al electrode, the active layer, PEDOT:PSS and ITO are observed. On the other hand, the additional layer with the thickness of several nm is observed between PEDOT:PSS and the active layer when PEG of 2mg is added. When amount of PEG is increased up to 8mg, the thickness of additional layer is increased to around 28 nm. Since the thickness of the additional layer increases proportionally with the amount of PEG, it is suggested that the PEG is segregated between the active layer and PEDOT:PSS layer during spin coating. It is similar to the result that the PEG layer is formed under the P3HT layer by the spontaneous phase separation when the blend of PEG and P3HT is spin coated [24]. The formation of the PEG layer under the active layer is also predicted [28], which is caused by the PEG high surface energy compared with PCBM and P3HT. The increase of J_{sc} would be due to the PEG layer formed between the active layer and PEDOT:PSS layer by the spontaneous phase separation which acts as a suitable hole transport layer to block the recombination of electron at the PEDOT:PSS/active layer interface.

In order to study the effect of PEG molecular weight, the similar organic solar cells were fabricated and tested using PEG with different molecular weight. Fig. 6 shows J_{sc} , V_{oc} , FF and PCE of solar cells with the molecular weight of 6000 for different amount of PEG. In contrast to the results of PEG 300, all the parameters get worse gradually with increasing the amount. With the increase of molecular weight, the degree of polymerization n ($HO - (CH_2 - CH_2) - O)_n - H$) increases. The gradual degradation is due to that the PEG interfacial is not formed under the active layer, or high resistance of PEG with large molecule, or the long PEG polymer is more tangled with P3HT chain. The further investigation is necessary to understand the behavior.

In order to clarify the effect of PEG layer as a hole transport layer, two kinds of

solar cells were fabricated by inserting the PEG layer (PEG 300) under the P3HT:PCBM active layer (Fig. 1(b)) and on the active layer (Fig. 1(c)), separately. The photovoltaic properties of these solar cells are compared with those without PEG in Table I. There is no remarkable difference in the V_{oc} by the insertion of PEG layer. On the other hand, the J_{sc} is increased by inserting the PEG layer between PEDOT:PSS layer and the active layer. On the contrary, the J_{sc} is decreased by inserting the PEG layer between the active layer and Al layer. The FF is improved with inserting the PEG layer. All these results are matching with the photovoltaic properties of P3HT:PCBM solar cell with adding PEG 300 in the blend of P3HT and PCBM during spin coating.

The stability of organic solar cell with PEG interfacial layer was tested with irradiating the solar light continuously. Fig. 7 plots the normalized PCE of P3HT:PCBM solar cells with PEG 300 (2mg) and without PEG. The figure indicates that degradation of solar cell was suppressed by using PEG. This is explained as follows. Main reason for the degradation of P3HT:PCBM solar cell is believed to be that the remained small amount of water in PEDOT:PSS is diffused to the Al electrode during the solar light irradiation, which make the electrode oxidization [29-31]. The degradation was minimized because the PEG layer becomes a barrier for water to diffuse. The more detailed characterization is needed to further improve the PCE and stability.

4. Conclusions

The PCE of P3HT:PCBM organic solar cell was improved by adding PEG with the molecular weight of 300 during spin coating. On the other hand, solar cell performance was degraded by adding PEG with the molecular weight of 6000. The effects of PEG amount on the photovoltaic properties of solar cell were indicated in detail. It was found that the J_{sc} and FF are improved by PEG, but the V_{oc} is not changed. The improvement was explained by the PEG layer formed by the spontaneous phase separation during spin coating. The degradation of solar cell was suppressed by PEG.

Acknowledgments

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References

1. H. Zhang, W. Y. Tan, S. Fladischer, L. Ke, T. Ameri, N. Li, M. Turbiez, E. Spiecker, X. H. Zhu, Y. Cao and C. J. Brabec, *J. Mater. Chem. A* **4**, 5032 (2016)
2. D. L. Morel, A. K. Ghosh, T. Feng, E. L. Stogrn, P. E. Purwin, R. F. Shaw and C. Fishman, *Appl. Phys. Lett.* **32**, 495 (1978)
3. C. W. Tang, *Appl. Phys. Lett.* **48**, 183 (1986)
4. M. Hiramoto, H. Fujiwara and M. Yokoyama, *Appl. Phys. Lett.* **58**, 1062 (1991)
5. S. E. Shaheen, C. J. Brabec, F. Padinger, T. Fromherz, J. C. Hummelen and N. S. Sariciftci, *Appl. Phys. Lett.* **78**, 841 (2001)
6. S. Uchida, J. Xue, B. P. Rand and S. R. Forrest, *Appl. Phys. Lett.* **84**, 421 (2004)
7. F. Padinger, R. S. Ritterberger and N. S. Sariciftci, *Adv. Funct. Mater.* **13**, 85 (2003)
8. Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. Mc Culloch, C. S. Ha and M. Ree, *Nat. Mater.* **5**, 197 (2006)
9. W. J. Belcher, K. I. Wagner and P. C. Dastoor, *Sol. Energy Mater. Sol. Cells* **91**, 447 (2007)
10. S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade and J. Hou, *Adv. Mater.* **28**, 9423 (2016)
11. F. Zhao, S. Dai, Y. Wu, Q. Zhang, J. Wang, L. Jiang, Q. Ling, Z. Wei, W. Ma, W. You, C. Wang and X. Zhan, *Adv. Mater.* **29**, 1700144 (2017)
12. X. Li, X. Liu, W. Zhang, H. Q. Wang and J. Fang, *Chem. Mater.* **29** (2017) 4176-4180.
13. A. J. Heeger, 25th Anniversary Article: *Adv. Mater.* **26**, 10 (2014)
14. D. M. Conzalez, V. Korstgens, Y. Yao, L. Song, G. Santoro, S. V. Roth and P. M. Buschbaum, *Adv. Energy Mater.* **5**, 1401770 (2015)
15. X. Zhang, Z. Li, Z. Zhang, S. Li, C. Liu, W. Guo, L. Shen, S. Wen, S. Qu and S. Ruan, *J. Phys. Chem.* **120**, 13954 (2016)
16. H. L. Yip and A. K. Y. Jen, *Energy Environ. Sci.* **5**, 5994 (2016) 5994
17. B. Qi, Z. G. Zhang and J. Wang, *Scientific Reports* **5**, 7803 (2015)
18. B. Kadem, W. Cranton and A. Hassan, *Organic Electronics* **24**, 73 (2015)
19. R. Steim, F. R. Kogler and C. J. Brabec, *J. Mater. Chem.* **20**, 2499 (2010)
20. T. Soga (ed), *Nanostructured Materials for Solar Energy Conversion* (Elsevier, Netherland, 2006), chapter 10, H. Hoppe and N. S. Sariciftci, pp. 277-318.
21. H. J. Kim, K. W. Seo, Y. J. Noh, S. I. Na, A. Sohn, D. W. Kim and H. K. Kim, *Sol.*

- Energy Mater. Sol. Cells **141**, 194 (2015)
22. R. Steim, S. A. Choulis, P. Schilinsky and C. Brabec, Appl. Phys. Lett. **92**, 093303 (2008)
 23. H. H. Liao, L. M. Chen, Z. Xu, G. Li and Y. Yang, Appl. Phys. Lett. **92**, 173303 (2008)
 24. I. Deckman, M. Moshonov, S. Obuchovsky, R. Brenner and G. L. Frey, J. Mater Chem. **A2**, 16746 (2014)
 25. S-C. Chen, F-C. Chen, M-K. Chung and C-S. Hsu, J. Phys. Chem. **116**, 1354 (2012)
 26. B. Qi and J. Wang, J. Mater. Chem. **22**, 24315 (2012)
 27. D. A. Mengistie, P-C. Wang and C-W. Chu, J. Mater. Chem. **A 1**, 9907 (2013)
 28. H. Kang, S. Kee, K. Yu, J. Lee, G. Kim, J. Kim, J. Kim, J. Kong and K. Lee, Adv. Mater, **27**, 1408 (2015)
 29. N. Norrman and F. C. Krebs, Sol. Energy Mater. Sol. Cells **90**, 213 (2006)
 30. K. Norrman, S. A. Gevorgyan and F. C. Krebs, ACS Appl. Mater. Interfaces **1**, 102 (2009)
 31. M. Wang, F. Xie, J. Du, Q. Tang, S. Zheng, Q. Miao, J. Chen, N. Zhao and J. B. Xu, Sol. Energy Mater. Sol. Cells **95**, 3303 (2011)

Figure Captions

Fig. 1. Structure of organic solar cells fabricated in this study; (a) the blend of P3HT, PCBM and PEG is spin coated, (b) the PEG layer is spin coated separately and the blend of P3HT and PCBM is spin coated on it and (c) the blend of P3HT and PCBM is spin coated and the PEG layer is spin coated on the active layer separately.

Fig. 2. Transmission spectra of organic solar cell structure with and without PEG.

Fig. 3. J-V characteristics of P3HT:PCBM organic solar cells with various amount of PEG 300.

Fig. 4. (a) The short circuit current density, (b) the open circuit voltage, (c) the fill factor and (d) PCE of P3HT:PCBM organic solar cells with various amount of PEG 300.

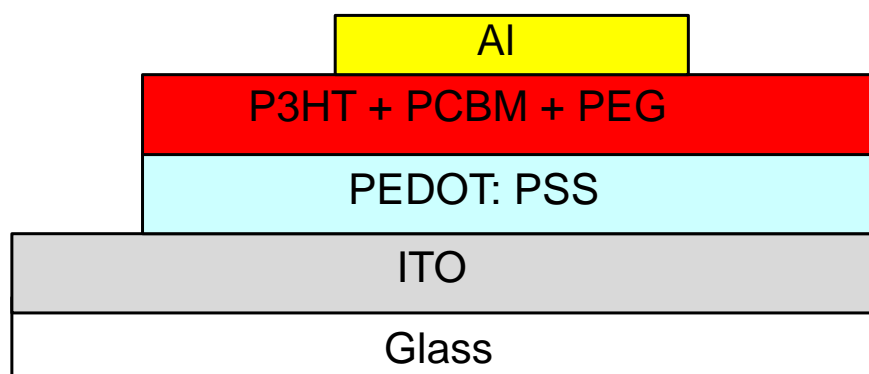
Fig. 5. Cross-sectional FE-SEM image of solar cell (a) without PEG, (b) with PEG 300 (2mg) and (c) with PEG 300 (8mg)..

Fig. 6. (a) The short circuit current density, (b) the open circuit voltage, (c) the fill factor and (d) PCE of P3HT:PCBM organic solar cell with various amount of PEG 6000.

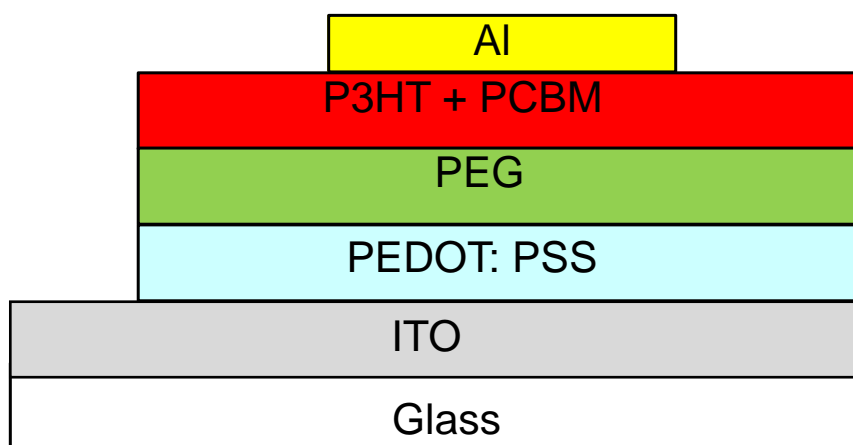
Fig. 7. Normalized PCE of P3HT:PCBM organic solar cells with and without PEG 300.

Table I. Photovoltaic properties of organic solar cells for different structures, (a) without PEG, (b) the PEG layer is inserted under the active layer and (c) the PEG layer is inserted on the active layer.

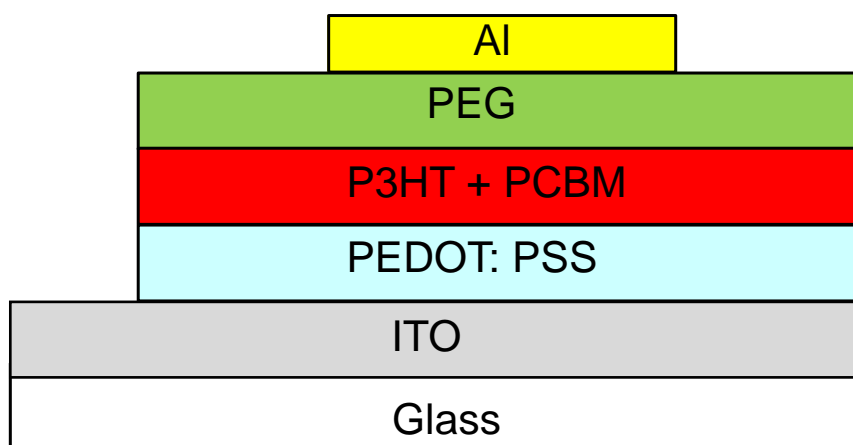
	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
Without PEG	0.55	7.42	0.62	2.54
With PEG (under active layer)	0.57	8.01	0.68	3.12
With PEG (on active layer)	0.55	6.63	0.65	2.38



(a)



(b)



(c)

Fig.1

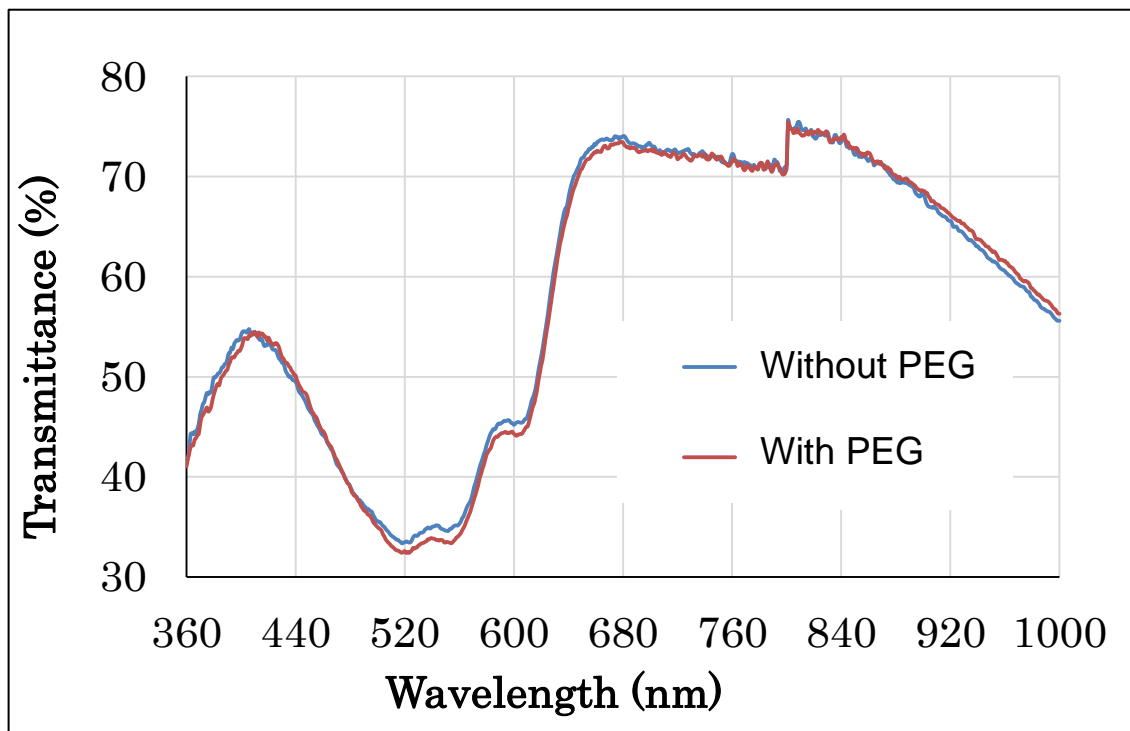


Fig. 2

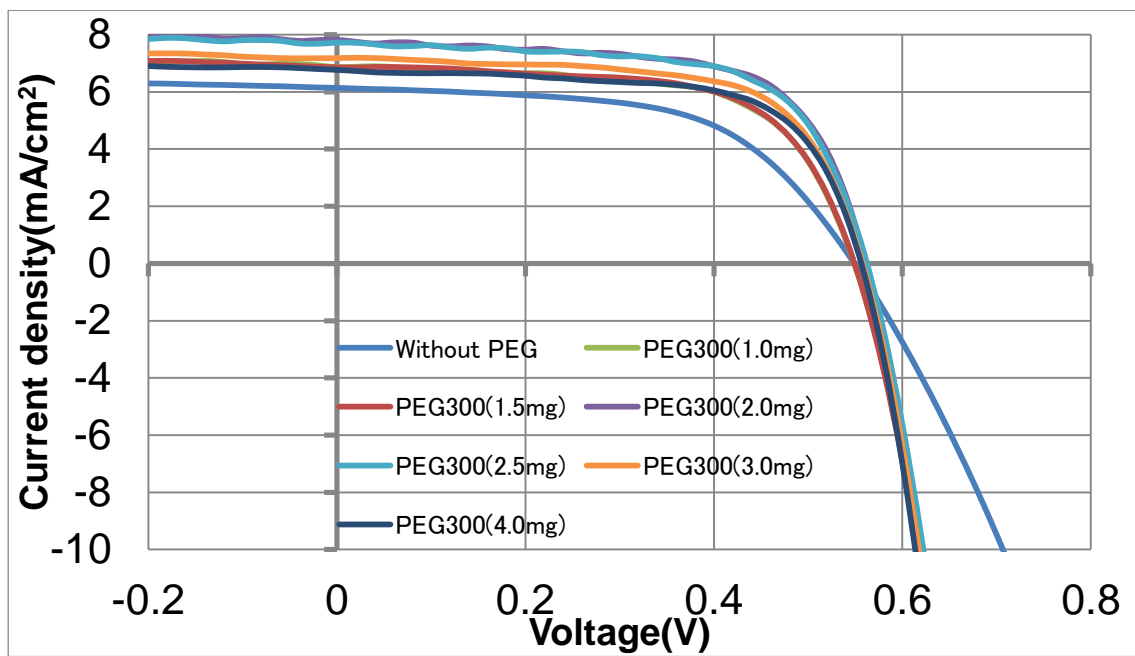


Fig. 3

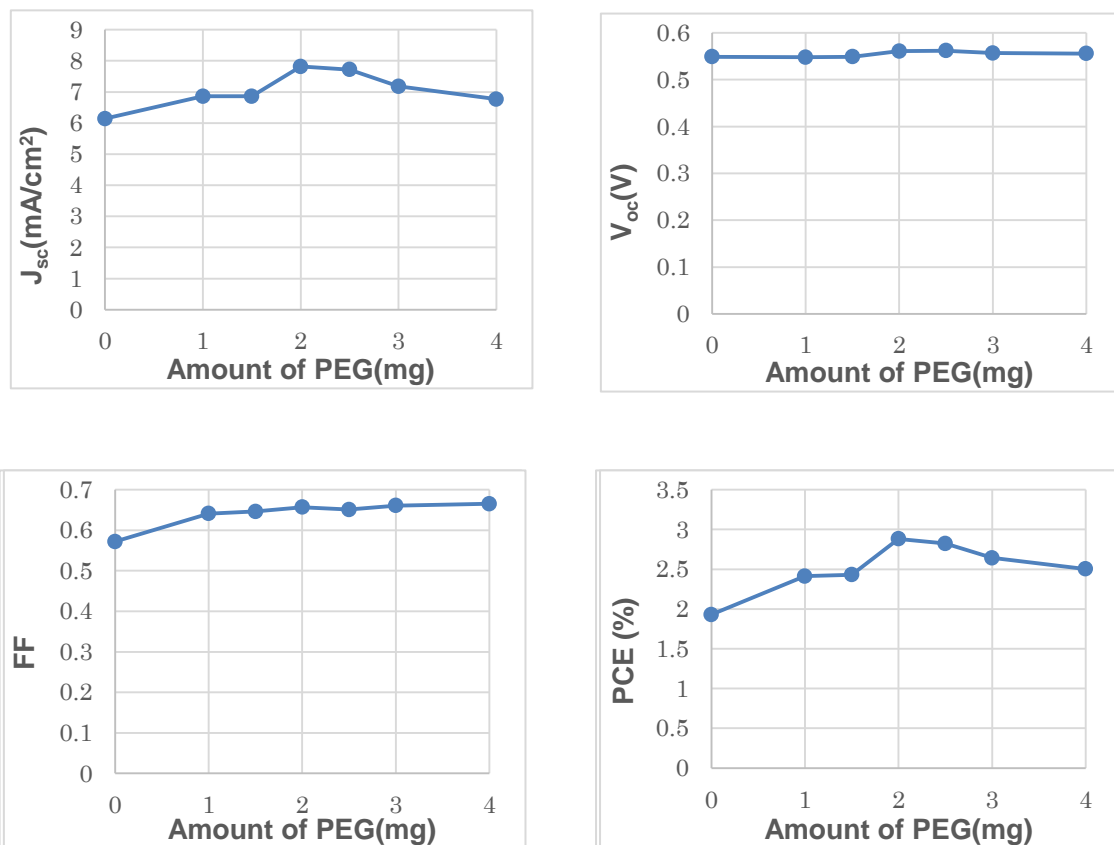
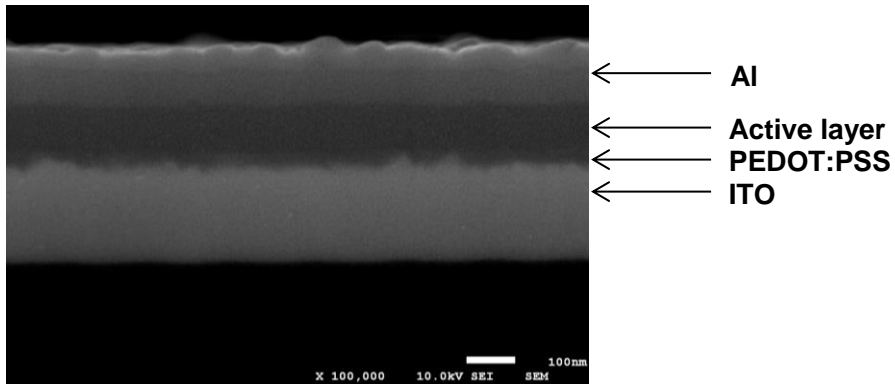
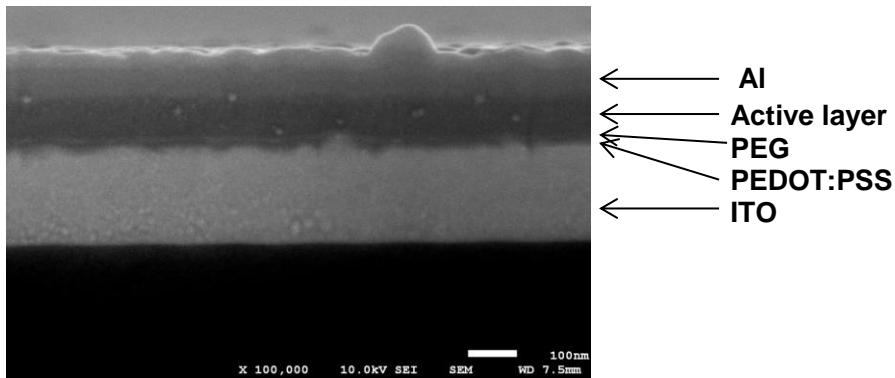


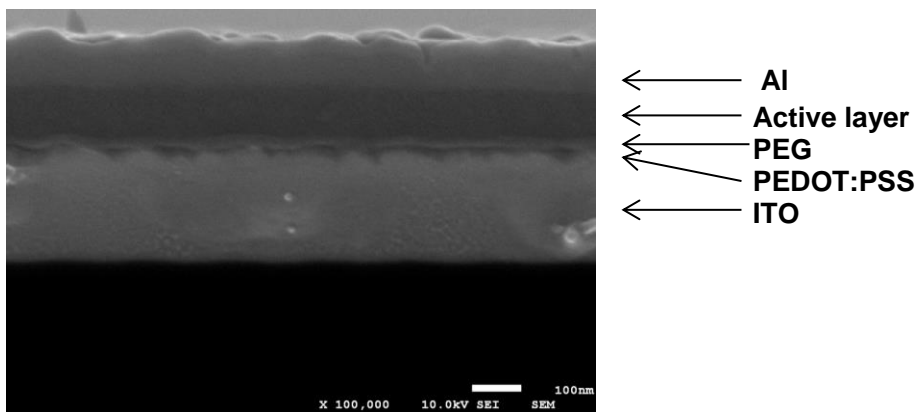
Fig.4



(a) without PEG



(b) with PEG (2 mg)



(c) with PEG (8 mg)

Fig. 5

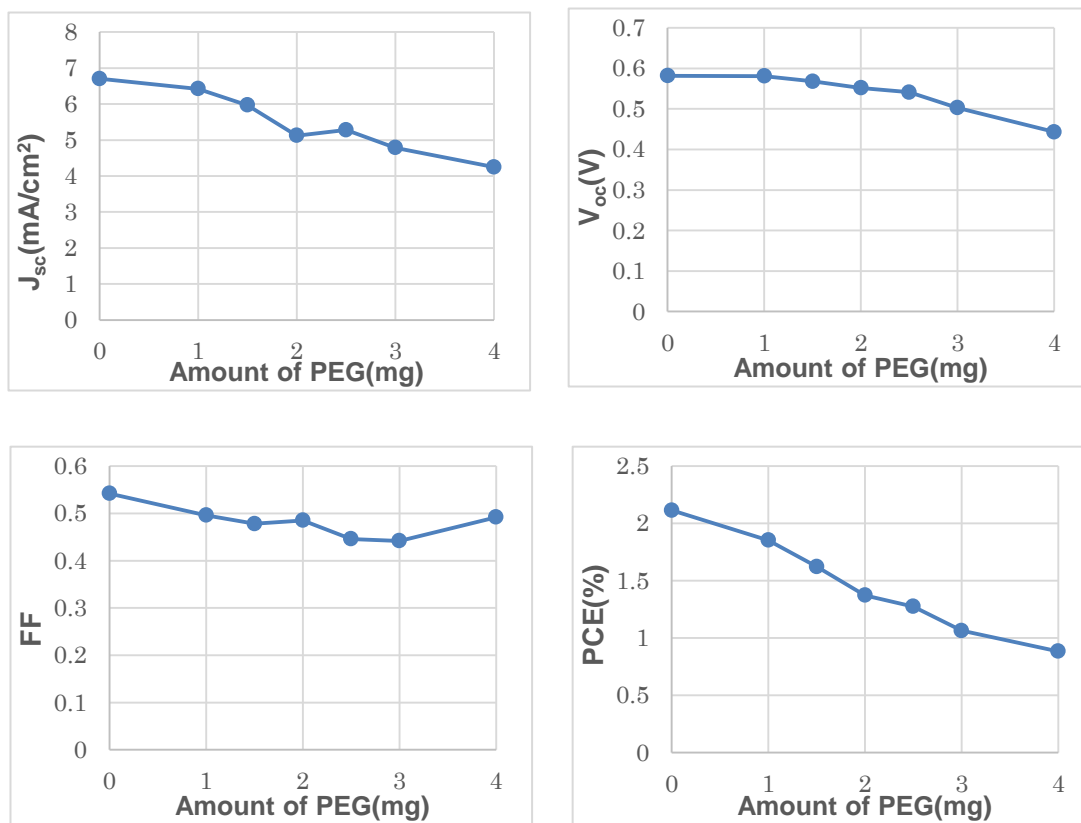


Fig. 6

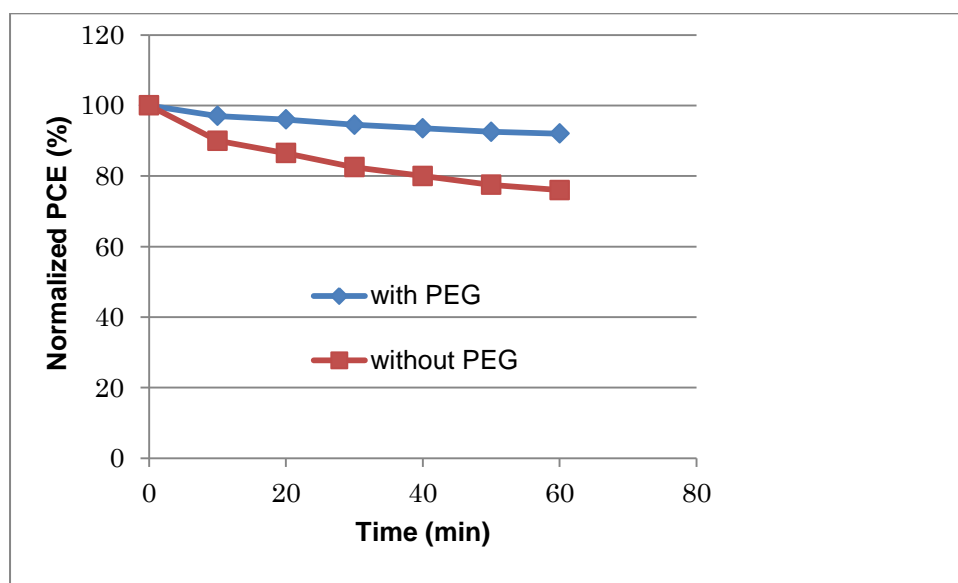


Fig. 7