

Effect of the solvent used to prepare the photoactive layer on the performance of inverted bulk heterojunction polymer solar cells

メタデータ	言語: eng 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	https://doi.org/10.24517/00010655

This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 International License.



Effect of the Solvent Used to Prepare the Photoactive Layer on the Performance of Inverted Bulk Heterojunction Polymer Solar Cells

Takayuki Kuwabara^{1,2,*}, Mitsuhiro Kuzuba¹, Natsumi Emoto¹, Takahiro Yamaguchi¹,
Tetsuya Taima^{1,2,3}, and Kohshin Takahashi^{1,2,*}

¹Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi,
Kanazawa, Ishikawa 920-1192, Japan

²Research Center for Sustainable Energy and Technology, Kanazawa University,
Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan

³JST-PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi,
Saitama 332-0012, Japan

The initial performance and subsequent degradation of inverted polymer solar cells (ITO/TiO_x/PCBM:P3HT/PEDOT:PSS/Au, TiO_x cell) is studied using photocurrent-voltage measurements combined with ac impedance spectroscopy (IS) and carrier mobility measurements. The TiO_x cells containing a P3HT:PCBM layer prepared from a solution of chlorobenzene (CB) showed a maximum power conversion efficiency (PCE) of 2.23%. In contrast, the TiO_x cells containing a P3HT:PCBM layer prepared from a solution of 1,2,3,4-tetrahydronaphthalene (Tetralin) containing 2 vol% 1,8-octanedithiol (ODT) exhibited a maximum PCE of 2.92%. However, after exposure to light irradiation for 100 h, the maximum PCE of the Tetralin:ODT cell decreased to 68% of its initial value. On the other hand, over 96% of the maximum PCE was maintained in the CB cell after 100 h of irradiation. IS measurements suggested that the degradation of the Tetralin:ODT cell was caused by a morphology change of the P3HT:PCBM layer that made efficient photoinduced charge separation difficult.

KEYWORDS: ac impedance spectroscopy, carrier mobility, durability, inverted polymer solar cells, solvent effect

*E-mail: tkuwabar@se.kanazawa-u.ac.jp

1. Introduction

Polymer solar cells have been attracting attention because of their potential to behave as a new electricity generating system that is low-cost, environmentally friendly, flexible, and lightweight¹⁻⁵). The power conversion efficiency (PCE) of polymer solar cells has recently reached close to 10%, because of the development of new *p*-conjugated polymers⁶⁻¹¹) and fullerene derivatives^{7,12}). The conjugated polymers contain stable quinoid resonance structures; for example, copolymers of benzodithiophene and thienothiophene, which absorb at long wavelength and possess a deep highest occupied molecular orbital level. Most of the studies on polymer solar cells to date have been devoted to improving the PCE, while much fewer have investigated stability and processing¹³⁻¹⁶).

There are various degradation processes derived from chemical and physical factors that affect the performance of polymer solar cells^{17,18}). For example, metal electrode materials such as Al are easily oxidized to an insulator with oxygen and water. In addition, the diffusion of Al into organic materials can create recombination sites for photoinduced carriers. The photoactive organic materials may be degraded by a photocatalytic effect at the material/oxide interface. Changes in the morphology of the photoactive layer may also be induced, causing the charge separation interface to decrease and degeneracy of the network structures used for carrier transport. However, the degradation mechanisms of polymer solar cells are not yet sufficiently understood.

Durable cells can be obtained using inverted solar cell geometry because the transparent metal oxide (e.g., amorphous titanium oxide TiO_x or zinc oxide ZnO) provides a noncorrosive electron collection electrode¹⁹⁻²³). We previously reported that the performance of an unsealed inverted polymer solar cell was maintained under continuous light irradiation for 100 h in an ambient atmosphere^{24,25}). We believe that this structure is a promising candidate to further improve the durability of polymer solar cells; in addition, it is also

possible to investigate the degradation mechanisms of such cells in detail²⁶⁻²⁹).

In this paper, the initial performance of inverted polymer solar cells (indium tin oxide (ITO) / amorphous titanium oxide (TiO_x) / [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM): regioregular poly(3-hexylthiophene) (P3HT) / poly(3,4-ethylenedioxythiophene): poly(4-styrene sulfonic acid) (PEDOT:PSS) / Au, denoted TiO_x cell) and their subsequent degradation mechanism have been investigated using photocurrent-voltage (*I-V*) characteristics combined with ac impedance spectroscopy (ac IS) and carrier mobility features. Effect of the solvent used to prepare the photoactive layer on the performance of inverted bulk heterojunction polymer solar cells is evaluated, allowing a degradation mechanism for inverted polymer solar cells to be proposed.

2. Experimental Section

2.1 Materials

Titanium(IV) oxysulfate (TiOSO₄), regioregular P3HT (Mw 87,000), PEDOT:PSS 1.3 wt% dispersion in water, polyoxyethylene tridecyl ether (PTE), chlorobenzene (CB), 1,2,3,4-tetrahydronaphthalene (Tetralin) and 1,8-octanedithiol (ODT) were purchased from Sigma-Aldrich Japan. Hydrogen peroxide (H₂O₂) was purchased from Kanto Chemical Co., Inc., Japan. PCBM was purchased from Frontier Carbon Co., Japan. All chemicals were used as received. ITO glass substrates (sheet resistance = 10 Ω/sq.), Au and Al wires were purchased from the Furuuchi Chemical Co., Japan.

2.2 Fabrication of inverted polymer solar cells

The ITO electrode was ultrasonicated in 2-propanol, cleaned in boiling 2-propanol, and then dried in air. An amorphous titanium oxide film (TiO_x) was prepared on the clean ITO substrate using a chemical bath deposition method as described in our previous paper²⁴). The

as-deposited TiO_x film on the ITO substrate was ultrasonicated for 10 min in water and then heated on a hot plate at 150 °C for 1 h in air. A solution of CB or Tetralin:ODT (98:2 by volume ratio) containing 25 g L⁻¹ P3HT and 20 g L⁻¹ PCBM (weight ratio of 5:4) was spin-coated onto the ITO/ TiO_x substrate at 700 rpm. When the Tetralin:ODT mixture was used, the as-prepared film was subsequently heated at 100 °C for 20 min on a hot plate. A dispersion of PEDOT:PSS in water containing 0.01 wt.% PTE was heated to 85 °C, and then spin-coated onto the P3HT:PCBM layer at 6000 rpm. The Au back electrode was vacuum deposited onto the PEDOT:PSS layer under a pressure of 2×10^{-5} Torr. The TiO_x cell is therefore described as ITO/ TiO_x /PCBM:P3HT/PEDOT:PSS/Au, and is shown in Figure 1a. Finally, the Tetralin:ODT cell prepared using a mixture of Tetralin:ODT and the CB cell prepared using CB were heated at 100 and 150 °C for 5 min in air, respectively, and then both cells were heated at 70 °C for 30 min. The effective area of each solar cell was restricted to 1.0 cm² by depositing the Au electrode through a shadow mask. All spin-coated films were prepared under a relative humidity of less than 35% at 25-35 °C in air.

2.3 Fabrication of hole-only devices

A dispersion of PEDOT:PSS in water was spin-coated onto a clean ITO electrode at 6000 rpm, and then dried at 150 °C for 5 min. A P3HT:PCBM layer, PEDOT:PSS layer and Au electrode were then sequentially fabricated on the PEDOT:PSS layer using the same method described in Section 2.2. All spin-coating procedures were carried out under a relative humidity of less than 35% at 25-35 °C in air. The structure of the hole-only device is described as ITO/PEDOT:PSS/PCBM:P3HT/PEDOT:PSS/Au, as shown in Figure 1b, and it has an effective area of 0.04 cm². Finally, the devices containing P3HT:PCBM layers prepared from solutions in Tetralin:ODT and CB were heated at 100 and 150 °C for 5 min, respectively, and then both cells were heated at 70 °C for 30 min in air.

2.4 Fabrication of electron-only devices

First, an Al layer was vacuum deposited on a clean ITO electrode at a pressure of 2×10^{-5} Torr. A P3HT:PCBM film was then prepared on the Al layer using the same method described in Section 2.2. An Al electrode was fabricated on the P3HT:PCBM layer by vacuum deposition at a pressure of 2×10^{-5} Torr. The structure of the electron-only device is described as ITO/Al/PCBM:P3HT/Al, as shown in Figure 1c, and it has an effective area of 0.04 cm^2 . Finally, the devices containing a P3HT:PCBM prepared from a solution of Tetralin:ODT or CB were heated at 100 and 150 °C for 5 min, respectively, and then both cells were heated at 70 °C for 30 min. All procedures were carried out in a glove box filled with N_2 that controlled the concentrations of both moisture and oxygen at less than 1 ppm to prevent corrosion of Al.

2.5 Measurements

The *I-V* characteristics of the solar cells were measured by linear sweep voltammetry (LSV) at a scan rate of 5 V min^{-1} under AM 1.5G simulated sunlight with an intensity of 100 mW cm^{-2} (equivalent to one sun). The light source was an XES-502S solar simulator (SAN-EI Electric, Japan) calibrated by an MS-601 pyranometer (EKO, Japan). The durability of the solar cells was tested using interval LSV measurements combined with open-circuit photovoltage measurements under continuous irradiation with simulated sunlight. All dc electric measurements were implemented using an HZ-5000 electrochemical analyzer (Hokuto Denko, Japan). Ac IS measurements were performed using a precision *LCR* meter 4284A (Hewlett-Packard, Japan) for solar cells in the dark and under simulated sunlight equivalent to one sun. The frequency range measured was from 20 Hz to 1 MHz, and the magnitude of the alternative signal was 5 mV. The obtained data were fitted with Scribner Associates Z-VIEW software v3.1 using appropriate equivalent circuits. Atomic force

microscopy (AFM) and UV-vis absorption spectrum were performed using a SII SPI3800N AFM (Seiko, Japan) and a U-3310 spectrophotometer (Hitachi, Japan), respectively. Measurements were mostly carried out in an ambient atmosphere, that is, at room temperature of 20-30 °C and under a relative humidity of 40-60 %; the *I-V* characteristics of the electron-only device were measured under an N₂ atmosphere to prevent the corrosion of Al.

3. Results and Discussion

3.1 Effect of the solvent used to prepare the P3HT:PCBM photoactive layer on the performance of polymer solar cells

Figure 2 shows *I-V* curves of the TiO_x cells containing P3HT:PCBM photoactive layers prepared from CB and Tetralin:ODT solutions, which are denoted CB and Tetralin:ODT cells, respectively. When CB was used as the solvent, the photocurrent gradually increased under light irradiation and the PCE reached 2.23% after 18 hours, resulting in a short-circuit photocurrent (J_{sc}) of 6.75 mA cm⁻², an open-circuit photovoltage (V_{oc}) of 0.58 V, and a fill factor (FF) of 0.57. In contrast, when Tetralin:ODT was used as the solvent, the photovoltaic feature was observed immediately after irradiation and the PCE reached 2.92% after a few minutes, resulting in a J_{sc} of 7.04 mA cm⁻², V_{oc} of 0.62 V, and FF of 0.67. The Tetralin:ODT cell showed a remarkably higher FF than the CB cell. The time to reach maximum PCE may represent the time required to maximize the velocity of electron transport from the electron acceptor PCBM in the photoactive layer to the electron collecting TiO_x layer. In our previous paper²³⁾, we analyzed the cause of the slow photoresponse of TiO_x cells using photo *I-V* and ac IS measurements. Such different initial behavior was caused by the condition of the surface of the electron collecting TiO_x layer because of variations in the electronic interaction between PCBM and TiO_x. However, electron transport from PCBM to TiO_x was improved by irradiating with UV light present in the simulated sunlight. That is,

PCBM molecules, which have partially polarized δ - carbonyl oxygen atoms, can approach photoaccumulated holes in the TiO_x layer of the Tetralin:ODT cell more closely than those in the TiO_x layer of the CB cell. This is because Tetralin has a much lower polarity than CB, which promotes interaction of PCBM with the TiO_x layer, and consequently the maximum PCE is obtained just after light irradiation.

To investigate the difference in the photovoltaic features, the properties of both active layers were measured by AFM and absorption spectra. Figure 3a and c shows surface AFM images of the P3HT:PCBM films prepared on ITO/ TiO_x substrates using CB and Tetralin:ODT solutions. The surface image of the PCBM:P3HT film prepared using Tetralin:ODT was much clearer than that of the blend film prepared using CB, although we cannot observe the morphology of the P3HT:PCBM layer. In addition, the absorption spectral shapes of both P3HT:PCBM films were almost same (not shown). It is known that absorption shoulder at around 600 nm derives from a crystallization of the P3HT. The result suggests that the crystallization of the blend film prepared using Tetralin:ODT is nearly equal to that of the blend film prepared using CB. Thus, such a result with combination of absorption spectra and film morphology is important for discussing the photocharge separation in detail. Instead of the direct observation, we estimated the carrier mobilities in the P3HT:PCBM films reflecting the morphology from the space charge limited current (SCLC) I - V characteristics of hole- and electron-only devices. I - V characteristics of hole-only and electron-only devices in the dark are shown in Figure 4. The SCLC behavior in the trap-free region can be characterized using the Mott-Gurney square law,

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \quad (1)$$

where J is the current density, ε_0 is the vacuum permittivity, ε_r is the dielectric constant of the organic material, μ is the carrier mobility, V is the applied voltage, and L is the thickness of

the organic film. ϵ_r was estimated to be 4 for P3HT and P3HT:PCBM from the electrostatic capacitance ($C = \epsilon_0\epsilon_r(S/L)$) deduced from ac IS measurements, and L was estimated from AFM measurements to be from 250 to 320 nm. By taking logarithmic conversion, above equation (1) becomes

$$\log J = 2\log V + \log\left(\frac{9}{8}\epsilon_r\epsilon_0\mu\frac{1}{L^3}\right) \quad (2)$$

and the μ can be written from equation (2)

$$\mu = \frac{8}{9} 10^{(\text{intercept})} L^3 \frac{1}{\epsilon_r \epsilon_0} \quad (3)$$

The carrier mobilities were calculated from the I - V curves in the square law region around 2-5 V, and the double-logarithmic plots of the I - V characteristics were fitted with a line with a slope of 2. The μ values were calculated by using the y intercept of the simulated line. The results of these calculations are summarized in Table I. Hole mobilities (μ_h) of $(3.3 \pm 0.1) \times 10^{-4}$ and $(8.5 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were obtained for P3HT layers prepared using CB and Tetralin:ODT, respectively, in the hole-only devices. The μ_h of the P3HT layer prepared using Tetralin:ODT was 2.6 times larger than that of the P3HT layer prepared using CB probably because of a greater degree of crystallinity in the P3HT layer. Furthermore, μ_h of $(2.1 \pm 0.5) \times 10^{-4}$ and $(1.2 \pm 0.3) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were obtained for P3HT:PCBM layers prepared using CB and Tetralin:ODT, respectively, in the hole-only devices. The μ_h of the blend layer prepared using Tetralin:ODT was 6 times larger than that of the blend layer prepared using CB probably because of the presence of a well-connected donor network. In contrast, the electron mobilities (μ_e) in the P3HT:PCBM layer prepared using CB and Tetralin:ODT were $(2.8 \pm 0.1) \times 10^{-3}$ and $(2.1 \pm 0.1) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the electron-only devices, respectively. The μ_e values were almost the same and were larger than the μ_h values. This shows that holes were the current-limiting carrier in both P3HT:PCBM blend films, and that the larger μ_h of the

blend prepared using Tetralin:ODT was responsible for the enhanced FF of the Tetralin:ODT cell.

3.2 Effect of solvent on the durability of polymer solar cells

The choice of solvent used to prepare a P3HT:PCBM photoactive layer is important not only for improving the PCE of TiO_x cells but also for maintaining their performance. Figure 5a shows the change in PCE with irradiation time in air for the unsealed CB and Tetralin:ODT cells, while Figure 5b and c show the time dependence of their normalized parameters (J_{sc} , V_{oc} , FF, and PCE). Over 96% of the maximum PCE of the CB cell was maintained, even under continuous irradiation with simulated sunlight equivalent to one sun, because the changes in J_{sc} , V_{oc} and FF were relatively small after reaching the maximum PCE, demonstrating that the CB cell is highly durable. In contrast, the maximum PCE of the Tetralin:ODT cell decreased to 68% of its initial value after irradiation for 100 h. This is mainly because the J_{sc} of the Tetralin:ODT cell decreased to 72% of its maximum value after 100 h.

We investigated the cause of the decrease in the J_{sc} by observing the surface of the blend films in the ITO/ TiO_x /PCBM:P3HT/PEDOT:PSS/Au cells before and after irradiation using AFM. The P3HT:PCBM surface was exposed by removing the PEDOT:PSS/Au layer using adhesive tape. The surface image of the CB cell was almost maintained before and after irradiation for 100 h, as shown in Figure 3a and b. On the other hand, the clear surface image of the Tetralin:ODT cell changed to an obscure image after irradiation for 100 h, as shown in Figure 3c and d. The result suggests that the morphology of the P3HT:PCBM layer prepared using Tetralin:ODT remarkably changed upon exposure to simulated sunlight for an extended period because of its metastable characteristic. To make sure that the change was indeed caused by the temperature increasing under continuous irradiation with simulated sunlight

containing infrared rays, the surface of the P3HT:PCBM films prepared using CB and Tetralin:ODT were investigated by AFM before and after heat treatment of the cells at 70 °C in the dark. As predicted, the surface image in the blend film prepared using Tetralin:ODT became obscure after heating continuously at 70 °C for 100 h in a similar manner to continuous exposure to simulated sunlight for 100 h, but the image of the blend film prepared using CB did not change. Furthermore after this heat treatment for 100 h, the PCE of the Tetralin:ODT cell decreased from 2.85 to 2.34%, while that of the CB cell remained almost unchanged (not shown).

To analyze the origin of the decay of J_{sc} in more detail, ac IS measurements were carried out for both cells. Figure 6 shows the time dependence of the Nyquist plots of the two cells under continuous irradiation from the equivalent of one sun at zero bias. The plots were analyzed using an equivalent circuit as shown in the inset of Figure 6a; the fitted curves show reasonable concordance with the experimental data. The plots for the CB and Tetralin:ODT cells were composed of two arcs at higher (>50 kHz) and lower frequency (<50 kHz), which are denoted as arcs 1 and 2, respectively. Arcs 1 and 2 were derived from the n-type TiO_x semiconductor and photoactive P3HT:PCBM layer, respectively^{20,21,23,30}. R_s represents the series resistance consisting of ohmic components, while R_1 and R_2 are resistance components forming a parallel circuit with constant phase elements denoted CPE1 and CPE2, respectively, as shown in the inset of Figure 6a. The CPEs are roughly equal to differential capacitances because there was almost no depression of the arcs. Figure 7 shows the time dependence of R_s , R_1 and R_2 of the CB and Tetralin:ODT cells under continuous irradiation from the equivalent of one sun. The R_s values of both cells were almost constant for 100 h. R_1 of the CB cell decreased rapidly from 126.2 $\Omega\text{ cm}^2$ in the dark to about 20 $\Omega\text{ cm}^2$ just after irradiation, and R_1 of the Tetralin:ODT cell decreased from 14.1 $\Omega\text{ cm}^2$ to about 3 $\Omega\text{ cm}^2$. Because R_1 represents the sum of the electrical resistance of the TiO_x bulk and both TiO_x

sides at the ITO/TiO_x and TiO_x/PCBM interfaces, its rapid decrease corresponds to the observed initial increase in PCE as discussed in Section 3.1. After the initial change, R1 of the CB and Tetralin:ODT cells remained almost constant at 9 and 2 Ω cm², respectively, under continuous irradiation for 100 h. On the other hand, R2, which represents the sum of the electrical resistance of the P3HT:PCBM bulk and P3HT:PCBM side at the TiO_x/PCBM:P3HT interface, increased gradually and monotonically after an initial rapid decrease. That is, R2 of the CB cell changed from 81,000 Ω cm² in the dark to 37.0 Ω cm² just after irradiation, and then to 62.1 Ω cm² after irradiation for 100 h. On the other hand, R2 of the Tetralin:ODT cell changed from 88,000 Ω cm² in the dark to 36.8 Ω cm² immediately after irradiation began, and then to 143.0 Ω cm² after irradiation for 100 h. The rapid decrease of R2 caused by exposure to light is caused by rapid generation of photocarriers in the P3HT:PCBM layer. It should also be noted that R2 of the Tetralin:ODT cell was 2.3 times larger than that of the CB cell after irradiation for 100 h. These ac IS results suggest that the observed decrease in PCE mainly originated from the gradual increase in R2 as the irradiation time increased. Because J_{sc} of the Tetralin:ODT cell decreased more rapidly than FF as shown in Figure 5c, we inferred that a rapid decrease of photocarriers in the photoactive blend layer during irradiation resulted in the increase of R2 of the Tetralin:ODT cell and consequently a large degradation in performance. The decrease of photocarriers is because of a morphology change in the active layer by heat generating upon exposure to simulated sunlight for an extended period.

4. Conclusions

Effect of the solvent used to prepare the P3HT:PCBM photoactive layer on the performance of polymer solar cells was investigated. The choice of solvent is important not only for improving the PCE of TiO_x cells but also for maintaining their performance. When Tetralin:ODT was used as a solvent to prepare the active layer, the PCE of the resulting cell

was 2.92%, and this value was 30% higher than that of the cell made using CB as the solvent. Furthermore, the time required to achieve the maximum PCE was a few minutes versus several hours for the Tetralin:ODT cell compared with the CB one. The larger PCE of the Tetralin:ODT cell is attributed to the increased hole mobility. In addition, the short time taken to reach maximum PCE is explained by differences in the interfacial distance between PCBM in the active layer and the electron-collecting TiO_x layer. That is, PCBM molecules with partially polarized δ - carbonyl oxygen atoms can approach photoaccumulated holes in the TiO_x layer of the Tetralin:ODT cell more closely than those in the TiO_x layer of the CB cell. This is because Tetralin has a much lower polarity than CB, consequently the maximum PCE is obtained soon after exposure to light. However, the durability of the Tetralin:ODT cell was lower under light irradiation in air than the CB cell. The decay in PCE is attributed to the decrease of the photo-produced charge carriers in the P3HT:PCBM bulk-heterojunction layer probably because of a morphology change in the active layer by heat generating upon exposure to simulated sunlight for an extended period. Thus, immobilization of the network of the active layer such as addition of cross-linkable materials and use of stable materials is important to develop highly durable polymer solar cells at a practical level.

Acknowledgments This work was supported by JSPS KAKENHI Grants-in-Aid for Scientific Research (B), for Young Scientists (A), and Exploratory Research. (Grant No. 24350092, 25708029, and 24655205, respectively), Japan.

References

- 1) B. Kippelen, J.-L. Bredas: *Energy Environ. Sci.* **2** (2009) 251.
- 2) J. Peet, A. J. Heeger, G. C. Bazan: *Acc. Chem. Res.* **42** (2009) 1700.
- 3) M. Helgesen, R. Sondergaard, F. C. Krebs: *J. Mater. Chem.* **20** (2010) 36.

- 4) I. Sasajima, S. Uesaka, T. Kuwabara, T. Yamaguchi, K. Takahashi: *Org. Electron.* **12** (2011) 113.
- 5) A. W. Hains, Z. Liang, M. A. Woodhouse, B. A. Gregg: *Chem. Rev.* **110** (2010) 6689.
- 6) Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu: *Adv. Mater.* **22** (2010) E135.
- 7) G. Zhao, Y. He, Y. Li: *Adv. Mater.* **22** (2010) 4355.
- 8) T.-Y. Chu, J. Lu, S. Beaupré, Y. Zhang, J.-R. m. Pouliot, S. Wakim, J. Zhou, M. Leclerc, Z. Li, J. Ding, Y. Tao: *J. Am. Chem. Soc.* **133** (2011) 4250.
- 9) Z. He, C. Zhong, X. Huang, W.-Y. Wong, H. Wu, L. Chen, S. Su, Y. Cao: *Adv. Mater.* **23** (2011) 4636.
- 10) S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You: *J. Am. Chem. Soc.* **133** (2011) 4625.
- 11) H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu, W. You: *Angewandte Chemie International Edition* **50** (2011) 2995.
- 12) Y.-J. Cheng, C.-H. Hsieh, Y. He, C.-S. Hsu, Y. Li: *J. Am. Chem. Soc.* **132** (2010) 17381.
- 13) L. Chang, H. W. A. Lademann, J.-B. Bonekamp, K. Meerholz, A. J. Moulé: *Adv. Funct. Mat.* **21** (2011) 1779.
- 14) L. Chang, I. E. Jacobs, M. P. Augustine, A. J. Moulé: *Org. Electron.* **14** (2013) 2431.
- 15) A. K. K. Kyaw, D. H. Wang, V. Gupta, J. Zhang, S. Chand, G. C. Bazan, A. J. Heeger: *Adv. Mater.* **25** (2013) 2397.
- 16) C. H. Peters, I. T. Sachs-Quintana, J. P. Kastrop, S. Beaupré, M. Leclerc, M. D. McGehee: *Advanced Energy Materials* **1** (2011) 491.
- 17) F. C. Krebs: *Sol. Energy Mater. Sol. Cells* **92** (2008) 715.

- 18) M. Jorgensen, K. Norrman, F. C. Krebs: Sol. Energy Mater. Sol. Cells **92** (2008) 686.
- 19) T. Kuwabara, T. Nakayama, K. Uozumi, T. Yamaguchi, K. Takahashi: Sol. Energy Mater. Sol. Cells **92** (2008) 1476.
- 20) T. Kuwabara, Y. Kawahara, T. Yamaguchi, K. Takahashi: ACS Appl. Mater. Interfaces **1** (2009) 2107.
- 21) T. Kuwabara, M. Nakamoto, Y. Kawahara, T. Yamaguchi, K. Takahashi: J. Appl. Phys. **105** (2009) 124513.
- 22) T. Kuwabara, H. Sugiyama, T. Yamaguchi, K. Takahashi: Thin Solid Films **517** (2009) 3766.
- 23) T. Kuwabara, C. Iwata, T. Yamaguchi, K. Takahashi: ACS Appl. Mater. Interfaces **2** (2010) 2254.
- 24) T. Kuwabara, H. Sugiyama, M. Kuzuba, T. Yamaguchi, K. Takahashi: Org. Electron. **11** (2010) 1136.
- 25) T. Kuwabara, T. Nakashima, T. Yamaguchi, K. Takahashi: Org. Electron. **13** (2012) 1136.
- 26) L. M. Chen, Z. Hong, G. Li, Y. Yang: Adv. Mater. **21** (2009) 1434.
- 27) K. Norrman, M. V. Madsen, S. A. Gevorgyan, F. C. Krebs: J. Am. Chem. Soc. **132** (2010) 16883.
- 28) M. Wang, Q. Tang, J. An, F. Xie, J. Chen, S. Zheng, K. Y. Wong, Q. Miao, J. Xu: ACS Appl. Mater. Interfaces **2** (2010) 2699.
- 29) T. Yang, W. Cai, D. Qin, E. Wang, L. Lan, X. Gong, J. Peng, Y. Cao: J. Phys. Chem. C **114** (2010) 6849.
- 30) T. Kuwabara, C. Tamai, Y. Omura, T. Yamaguchi, T. Taima, K. Takahashi: Org. Electron. **14** (2013) 649.

Table I Carrier mobilities in P3HT and P3HT:PCBM layers prepared using CB or Tetralin:ODT as the solvent.

Organic layer	Solvent	$\mu_h / \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	$\mu_e / \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$
P3HT	CB	$3.3 \pm 0.1 \times 10^{-4}$	-
	Tetralin:ODT	$8.5 \pm 0.1 \times 10^{-4}$	-
P3HT:PCBM	CB	$2.1 \pm 0.5 \times 10^{-4}$	$2.8 \pm 0.1 \times 10^{-3}$
	Tetralin:ODT	$1.2 \pm 0.3 \times 10^{-3}$	$2.1 \pm 0.1 \times 10^{-3}$

Figure captions

Figure 1 Schematic diagram showing the structure of inverted polymer solar cells (a), hole-only device (b) and electron-only device (c).

Figure 2 Photo I - V curves of inverted polymer solar cells containing P3HT:PCBM blend films prepared from solutions of chlorobenzene (CB) or 1,2,3,4-tetrahydronaphthalene:1,8-octanedithiol (Tetralin:ODT) under irradiation with simulated sunlight equivalent to one sun.

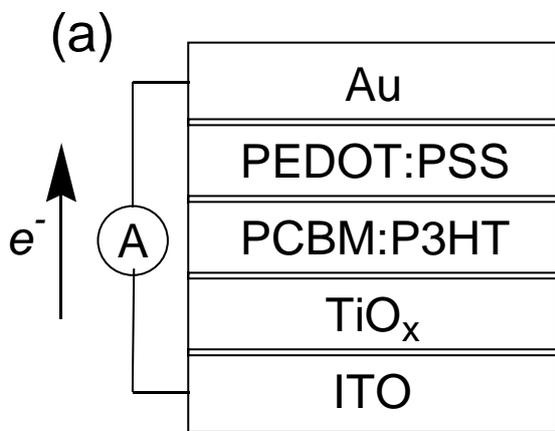
Figure 3 AFM images of the surface of the P3HT:PCBM layers of the CB (a, b) and Tetralin:ODT (c, d) cells. Before (a, c) and after (b, d) irradiation with simulated sunlight equivalent to one sun for 100 h.

Figure 4 Double-logarithmic plots of I - V curves obtained for hole-only devices (ITO/PEDOT:PSS/PCBM:P3HT/PEDOT:PSS/Au) (a) and electron-only devices (ITO/Al/PCBM:P3HT/Al) (b) in the dark. The thickness of the blend films is 250-320 nm. Solvents used to prepare the P3HT:PCBM films: CB (\square) and Tetralin:ODT (\circ). The solid lines are simulated lines with slope = 2.

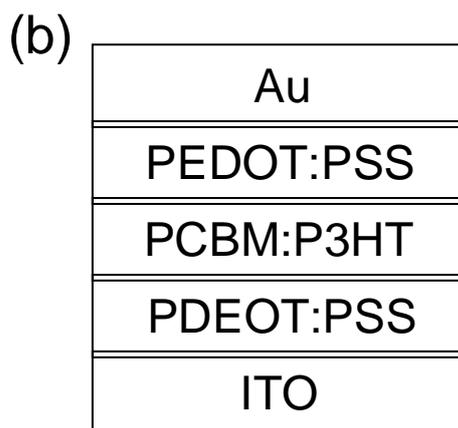
Figure 5 (a) Time dependence of the PCE values of inverted polymer solar cells containing P3HT:PCBM blend films prepared using CB (●) and Tetralin:ODT (○) under irradiation with simulated sunlight equivalent to one sun. Time dependence of normalized parameters of CB (b) and Tetralin:ODT cells (c). Parameters: Normalized J_{sc} (□), V_{oc} (○), FF (△), and PCE (×).

Figure 6 Time dependence of the Nyquist plots of CB (●) and Tetralin:ODT (○) cells under irradiation with simulated sunlight equivalent to one sun at zero bias. The solid lines are lines of best fit calculated using equivalent circuits. The inset illustrates a typical equivalent circuit for the Nyquist plots containing two arcs. R_s : series resistance consisting of the ohmic components, R_1 and R_2 : resistances, CPE_1 and CPE_2 : capacitances.

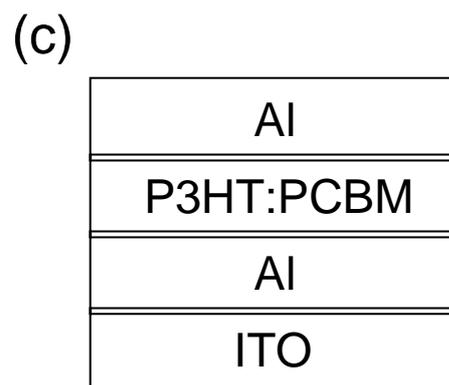
Figure 7 Time dependence of R_s (a), R_1 (b), and R_2 (c) values for the CB (●) and Tetralin:ODT (○) cells under irradiation with simulated sunlight equivalent to one sun.



Inverted polymer solar cell



Hole-only device



Electron-only device

Figure 1

Kuwabara et al.

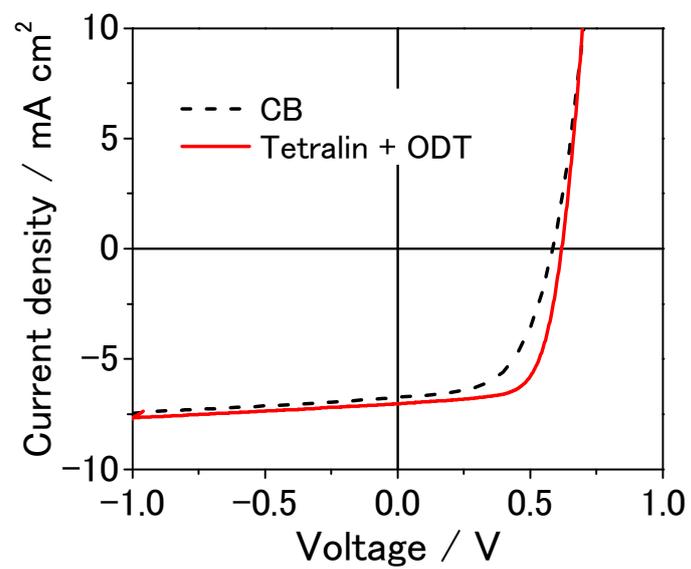


Figure 2

Kuwabara et al.

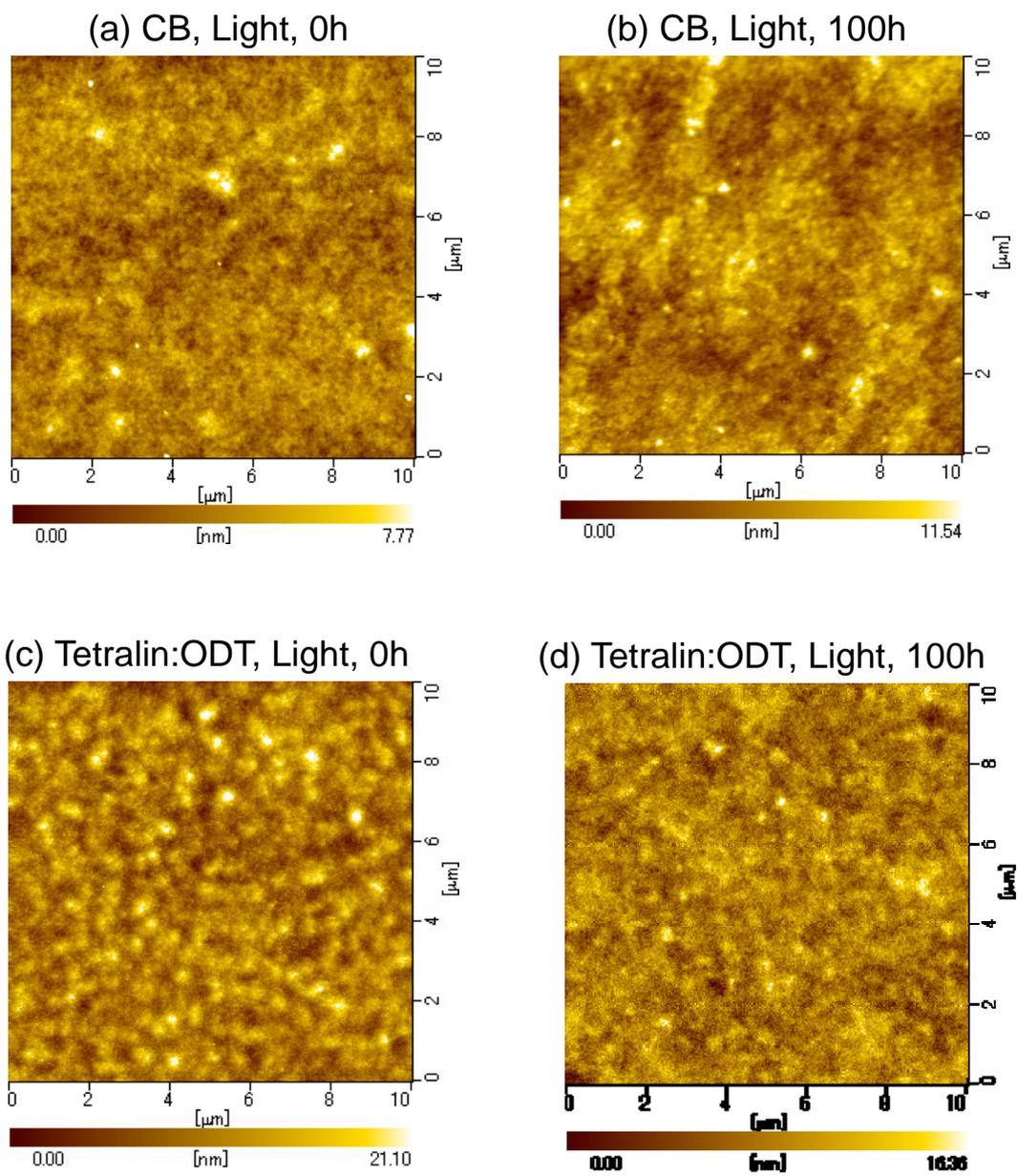


Figure 3

Kuwabara et al.

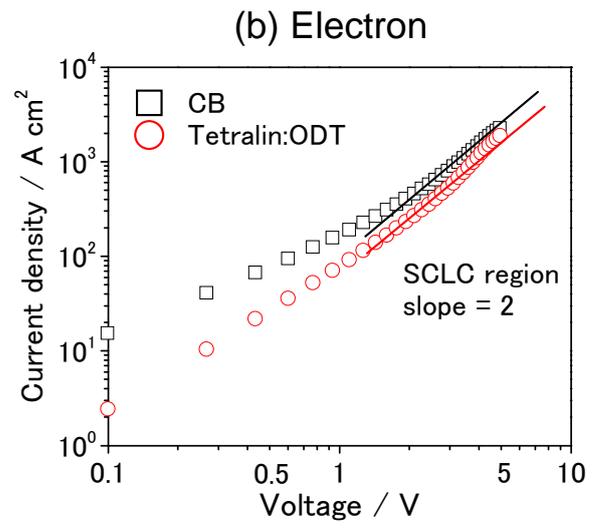
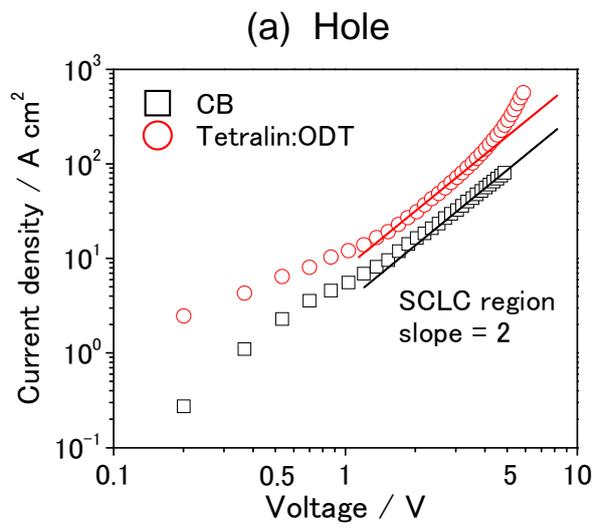


Figure 4

Kuwabara et al.

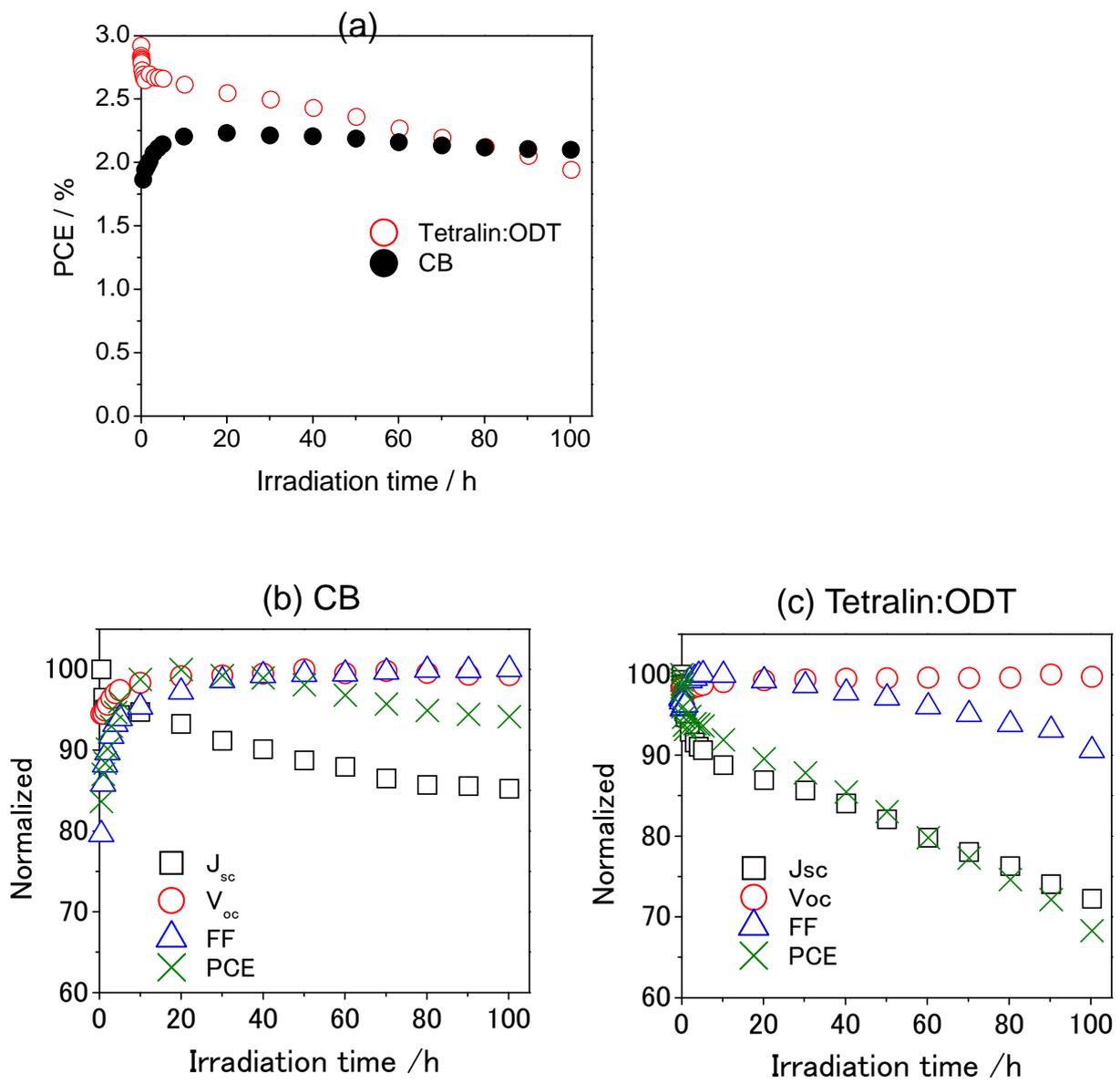


Figure 5

Kuwabara et al.

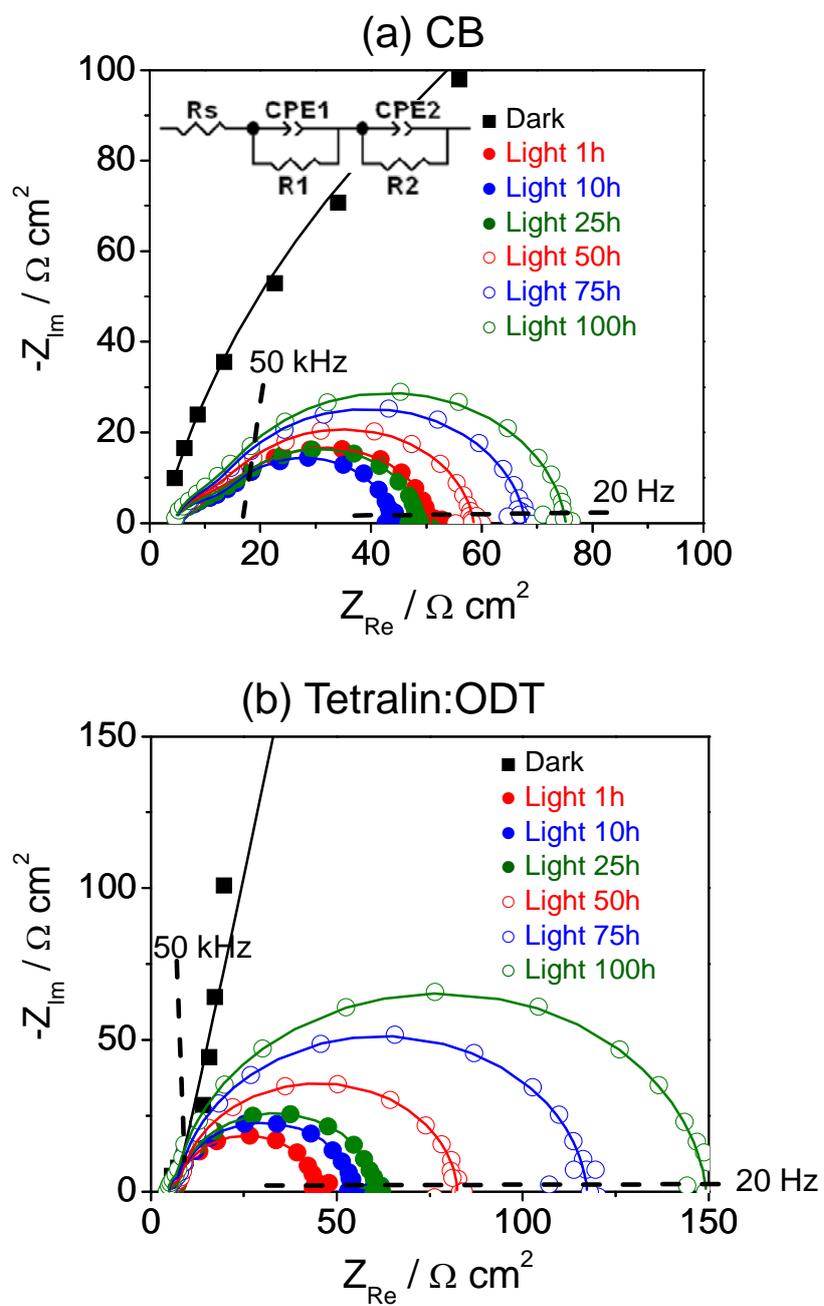


Figure 6

Kuwabara et al.

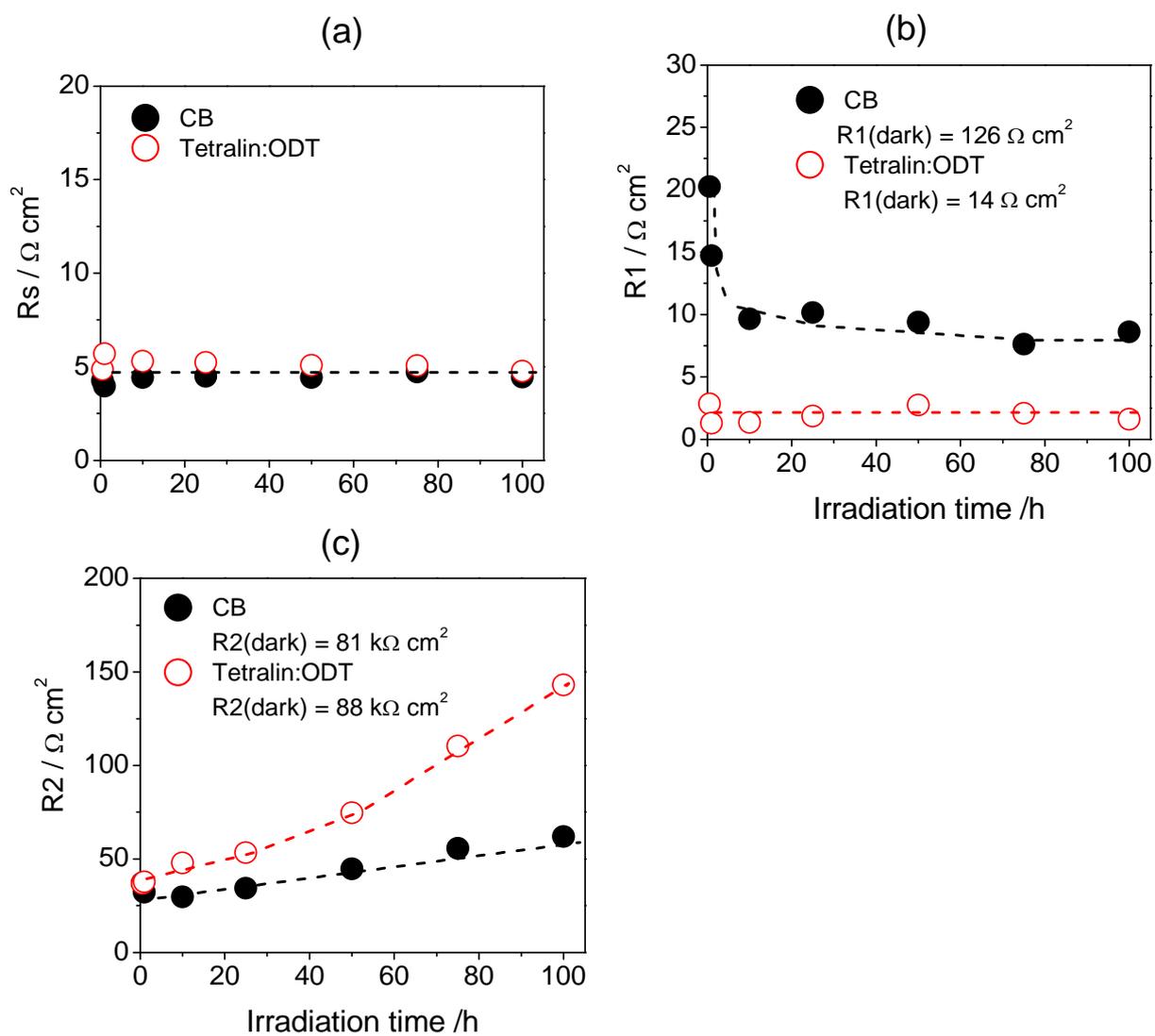


Figure 7

Kuwabara et al.