

Solid-state dye-sensitized TiO₂ solar cells using poly(3,4-ethylenedioxythiophene) as substitutes of iodine/iodide electrolytes and noble metal catalysts on FTO counter electrodes

Yukyeong Kim^{a,b}, Yung-Eun Sung^a, Jiang-Bin Xia^b, Monica Lira-Cantu^c,
Naruhiko Masaki^b, Shozo Yanagida^{b,*}

^a School of Chemical and Biological Engineering, Seoul National University, San56-1, Sillim-dong, Gwanak-gu, Seoul 151-744, Republic of Korea

^b Center for Advanced Science and Innovation, Osaka University, Yamadaoka2-1, Suita, Osaka 565-0871, Japan

^c Institut De Ciencia de Materials de Barcelona, Campus de la UAB, E-08193 Bellaterra, Spain

Received 7 February 2007; received in revised form 18 May 2007; accepted 11 June 2007

Available online 14 June 2007

Abstract

Solid-state dye-sensitized TiO₂ solar cells using commercially available ruthenium dye (Z907) as an hydrophobic sensitizing dye and poly(3,4-ethylenedioxythiophene) (PEDOT) as a hole conductor and a platinum-free counter electrodes were fabricated. The nanospace of the dyed TiO₂ layer was filled with PEDOT through the *in situ* photoelectrochemical polymerization of bis-ethylenedioxythiophene (bis-EDOT). In this study, we revealed several factors for the photoelectrochemical polymerization and obtained the conversion efficiency of 2.6% with high open circuit voltage over 0.8 V.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Photoelectrochemical polymerization; PEDOT; Solid-state dye-sensitized solar cells

1. Introduction

As for dye-sensitized TiO₂ solar cells (DSC) introduced by O'Regan and Grätzel in 1991 [1], more than 10% conversion efficiency has been achieved with novel ideas and through intensive researches. Many advantages such as low production cost and diversity in manufactures have made DSC promising as next-generation photovoltaic devices. On the other hand, DSC faces high-temperature stability issue (>85 °C) to pass standardized packaging durability tests of solar cells. One of the solutions is the solidification of DSC using iodine-free organic hole-conducting materials such as solid organic hole conductors [2–6] and conducting conjugated polymers [7–9]. The highest conversion efficiency of 4% achieved using spiro-MeOTAD as a hole conductor [3]. The important factor to achieve the high performance is the optimum filling of pore spaces of mesoscopic electrodes with the hole-conducting material.

We recently reported that PEDOT works as an excellent hole-conductor like iodide/iodine electrolytes. The *in situ* photoelectrochemical polymerization of bis-EDOT was elucidated to be one effective way to fill the nano-size pore spaces of the TiO₂ electrodes with hole-conducting PEDOT [10–12]. Herein taking into account the excellent electron transfer catalysis of PEDOT on fluorine-doped SnO₂ (FTO) likewise platinum or gold [13], we present the optimization studies of photoelectrochemical polymerization of bis-EDOT using commercially available ruthenium complex dye (Z907).

2. Experimental

The solar cell device is composed of FTO with compact TiO₂ layer (CL) as a conducting substrate, dyed nanoporous TiO₂ as a photoactive layer and PEDOT as a hole-conducting material and as a substitute of Pt counter electrode. To avoid electron leakage through the direct electrical contact of FTO and the *in situ* formed PEDOT, the compact TiO₂ as an electron blocking layer was introduced by spin coating method [14].

* Corresponding author. Tel.: +81 6 6879 7351; fax: +81 6 6879 7351.
E-mail address: yanagida@mls.eng.osaka-u.ac.jp (S. Yanagida).

The commercially available Nanoxide-T paste (Solaronix) was used for fabrication of nanoporous TiO₂ layer. The 7 μm thick TiO₂ layer on the blocking-layered FTO were prepared by twice doctor blade coating and sintered at 450 °C for 30 min. The resulting TiO₂ electrode was immersed into 3 × 10⁻⁴ M solution of *cis*-RuLL'(NCS)₂ (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, L' = 4,4'-dinonyl-2,2'-bipyridine, NCS = isocyanato: Z907, Solaronix) with and without deoxycholic acid (DCA) in 50:50 mixture of acetonitrile and *tert*-butanol by volume for 4 h at 65 °C. The dye adsorbed TiO₂ electrode was fully immersed into the solution composed of 0.01 M bis-EDOT and 0.1 M LiClO₄ in acetonitrile. Through the TiO₂ anode side illumination [11] using white light with UV-cut and 25% neutral density filters (30 mW/cm², λ > 500 nm) and using chronoamperometry (potentiostat: BAS 100B), photoelectrochemical polymerization of bis-EDOT was carried out. The dyed TiO₂ film was used as a working electrode and Pt wire as a counter electrode and Ag/AgCl as a reference electrode for electrochemical process.

After *in situ* photoelectrochemical polymerization, the resulting TiO₂/dye/PEDOT electrode was rinsed using ethanol and dried, and then 1 drop of BMImTFSI (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide) with 0.2 M of tBP (4-*tert*-butylpyridine) and 0.2 M of LiTFSI (lithium bis(trifluoromethanesulfonyl)amide) was added on the surface. The photoelectrode of TiO₂/dye/PEDOT was kept in the dark place for 24 h before measurements. As a cathode, PEDOT was prepared on FTO by chronoamperometry of 0.8 V for 180 s using the same electrolyte. A sandwich-type cell of FTO/CL/TiO₂/Dye/PEDOT-PEDOT/FTO was assembled using clips. The photoenergy conversion efficiency was measured using simulated light of 100 mW/cm² with AM 1.5 (YSS-80, Yamashita Denso) at room temperature. The incident photon-to-current conversion efficiency (IPCE) was obtained using monochromic light of 5 mW/cm² (PV-25DYE, JASCO).

3. Results and discussions

Photoelectrochemical polymerization is initiated by the photo-excitation of the Z907 dye molecules on the TiO₂ under visible light irradiation. The oxidized dye gives an active site to polymerize bis-EDOT to PEDOT presenting a good contact of the hydrophobic Z907 molecules and the hole-conducting PEDOT at the interface. In this study, we investigated the effect of the applied potential and reaction time on *in situ* photoelectrochemical polymerization and the effect of deoxycholic acid (DCA) as a co-adsorbent of Z907 on the *in situ* photoelectrochemical polymerization and photon-to-electron energy conversion efficiency.

First, the effect of DCA as a co-adsorbent of Z907 during dye adsorption was examined. During dye adsorption to the TiO₂ surface, some dye molecules aggregate with each other on the TiO₂ surface, resulting in lower efficiency. To prevent dye aggregation, acids with carboxylate or phosphonate groups which can be strongly anchored on the TiO₂ surface are used as co-adsorbents of the dye molecules [15–17]. To verify the effect of co-adsorbent, four kinds of dye solutions with different concentration ratio of DCA as a co-adsorbent were prepared; the molar

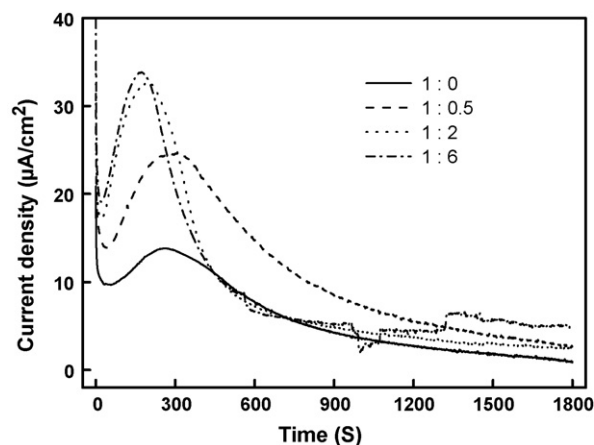


Fig. 1. Current–time curves of *in situ* photoelectrochemical polymerization: the effect of concentration ratio of Z907 to DCA in the dye adsorption, chronoamperometry of 0.2 V vs. Ag/AgCl (the labels represent molar ratio of Z907 to DCA in the dye solution).

ratio of Z907 to DCA is 1:0, 1:0.5, 1:2 and 1:6. Z907 molecules and DCA adsorbed on the TiO₂ surface competitively during dye adsorption process. Fig. 1 shows the current–time curves of photoelectrochemical polymerization of bis-EDOT at 0.2 V versus Ag/AgCl for 1800 s; the current increased at the beginning more rapidly in the case of co-adsorbent and dye mixture adsorbed TiO₂ than pure dye adsorbed TiO₂ film. And the total polymerization charge also increased as increasing the concentration ratio of co-adsorbent, DCA. In photoelectrochemical polymerization, bis-EDOT starts to grow on the oxidized dye molecule. The aggregated dyes on the TiO₂ surface provide relatively small number of active sites due to crowded narrow space compared with non- (or less) aggregated dyes on TiO₂, and smaller size of co-adsorbent attached on the TiO₂ surface could provide more effective space for initiation and propagation of polymerization. Fig. 2 shows *I*–*V* curves of the assembled cells using photoelectrode of TiO₂/DCA-Z907/PEDOT obtained from Fig. 1 with different concentration ratio of DCA to Z907. The higher efficiency could be obtained when more than double amount of

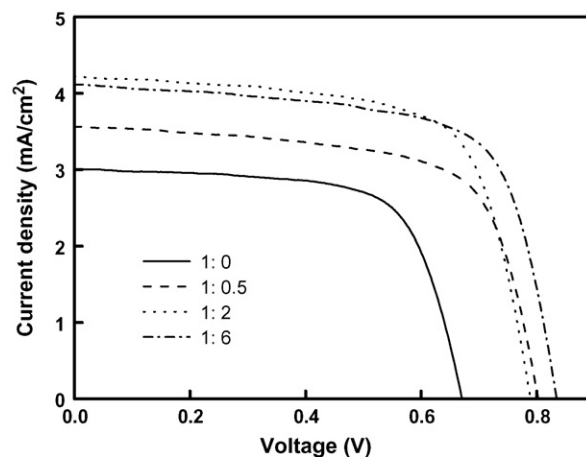


Fig. 2. *I*–*V* curves of the assembled solar cells: the effect of concentration ratio of Z907 to DCA in the dye adsorption (the labels represent molar ratio of Z907 to DCA in the dye solution).

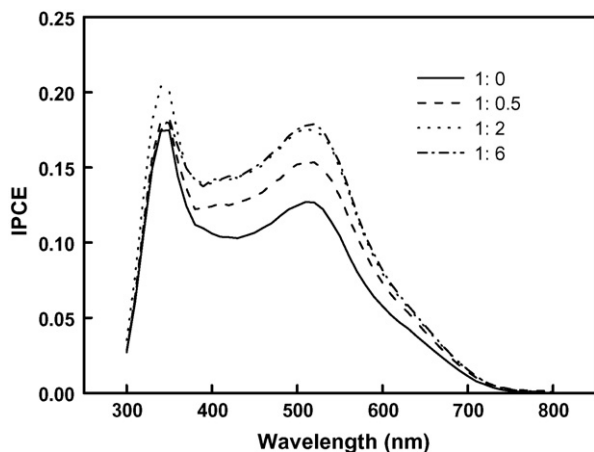


Fig. 3. IPCE curves of the assembled solar cells: the effect of concentration ratio of Z907 to DCA in the dye adsorption (the labels represent molar ratio of Z907 to DCA in the dye solution).

DCA to Z907 was used. Fig. 3 shows IPCE data of a series of the assembled cells.

Secondly, the effect of the electric field and reaction time of photoelectrochemical polymerization was examined. Fig. 4 shows the cyclic voltammetry of bis-EDOT using the same electrolyte. The bare FTO, Pt wire and Ag/AgCl was used as a working, counter and reference electrode, respectively. Fig. 4 indicates that bis-EDOT starts to be deposited electrochemically around 0.75 V. Then the potential of *in situ* photoelectrochemical polymerization was applied from 0.1 to 0.6 V with the fixed time and using dyed TiO₂ prepared using the dye solution (Z907:DCA, 1:2). Under visible light irradiation the oxidation of the dye molecules occurs and the potential of oxidized dye molecules is higher than one applied by potentiostat. For *in situ* photoelectrochemical polymerization, LiClO₄ was used as a supporting electrolyte and the perchlorate anion (ClO₄⁻) acts as a dopant, i.e., counter anion of the oxidized PEDOT state. The different applied potential provides different electric field in electrochemical system influencing the migration of redox couples. The current–time curves with different applied potentials are shown in Fig. 5, indicating that the current peak is

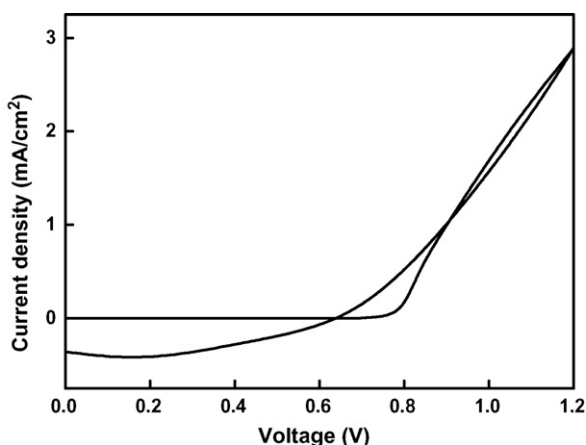


Fig. 4. Cyclic-voltammetry of bis-EDOT with scan rate of 20 mV/s using electrolyte of 0.01 M of bis-EDOT and 0.1 M of LiClO₄ in acetonitrile.

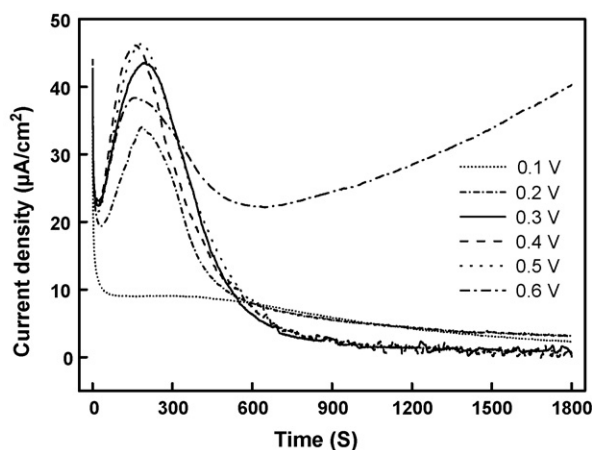


Fig. 5. Current–time curves of *in situ* photoelectrochemical polymerization with various applied potentials using co-adsorbent and dye mixture adsorbed TiO₂ electrode prepared from the dye solution (Z907:DCA, 1:2).

deeper at higher applied potential and the polymerization charge increased with increasing applied potential. The high electric field accelerates reactivity of bis-EDOT and increases migration of anion, ClO₄⁻ therefore PEDOT grew not only on the oxidized dye molecules but also on any sites on the anode. When 0.6 V was applied, the current rapidly increased again after 600 s. This was originated from direct electrodeposition on the substrate and slightly blue color on the compact TiO₂ layer was detected. The assembled cell using this TiO₂/dye/PEDOT (at 0.6 V) electrode was not operated because of the short circuit. The optimum applied potential window was confirmed to be between 0.2 and –0.3 V from the *I*–*V* curves in Fig. 6. At the above 0.4 V applied potential, the open circuit voltage and the fill factor decreased. And the effect of *in situ* polymerization time was examined with the fixed applied potential (0.2 V) and dye solution (Z907:DCA, 1:2). The photoelectrochemical polymerization was stopped at the chosen time of 300, 600, 1200, and 1800 s. The highest performance was obtained from the sample of 1200 s not from the one of 1800 s with higher polymerization charge (listed in Table 1). The optimum photoelectrochemical polymerization time window would be different depending on

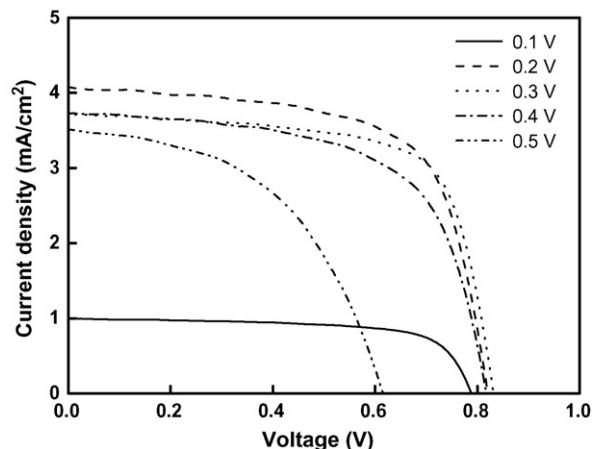


Fig. 6. *I*–*V* curves of the assembled solar cells: the effect of applied potential on *in situ* photoelectrochemical polymerization.

Table 1

The charge of *in situ* photoelectrochemical polymerization and the photovoltaic performance of the assembled cells: the effect of photoelectrochemical polymerization times at the fixed applied potential of 0.2 V using co-adsorbent and dye mixture adsorbed TiO₂ electrode prepared from the dye solution (Z907:DCA, 1:2)

Time (s)	300	600	1200	1800
Charge of polymerization (mC/cm ²)	8.6	12.8	15.8	16.9
V _{oc} (V)	0.88	0.83	0.85	0.86
J _{sc} (mA/cm ²)	2.21	4.18	4.48	4.10
Fill factor	0.68	0.70	0.69	0.67
Efficiency (%)	1.32	2.42	2.62	2.39

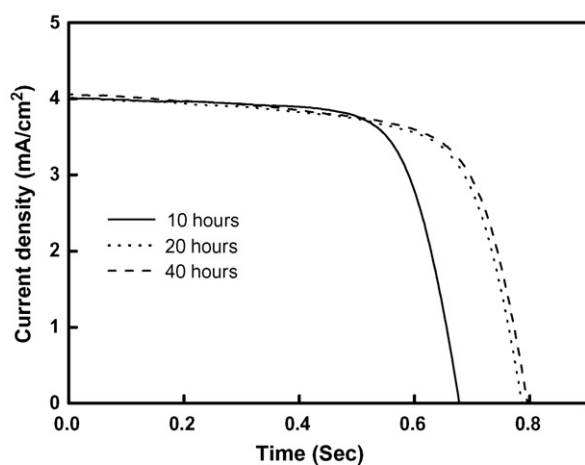


Fig. 7. *I*–*V* curves of the assembled solar cells: the effect of treatment time of the ionic liquid mixture of BMImTFSI, tBP and LiTFSI.

the applied potential and the state of adsorbed dye molecules on the TiO₂ surface and vice versa.

Finally, the effect of the treatment time of the ionic liquid mixture of BMImTFSI and tBP and LiTFSI after adding it onto the TiO₂/dye/PEDOT electrode was examined. The ionic liquid improves the dark current property of the cells, being accompanied by the increase of the open circuit voltage and the fill factor in photocurrent characteristics [18–20]. Fig. 7 shows the photovoltaic performances with the ionic liquid treatment time of 10, 20, and 40 h using photoelectrode of TiO₂/dye/PEDOT prepared using the fixed dye solution (Z907:DCA, 1:2) and under photoelectrochemical polymerization condition of 0.2 V applied potential for 1800 s. For deep penetration at least 20 h is needed because of the high viscosity of the ionic liquid mixture and the results reported here were all obtained after 24 h treated with the ionic liquid mixture as mentioned in the experimental section.

4. Conclusions

In situ photoelectrochemical polymerization of bis-EDOT is an effective way to fill the pore of dyed nanoporous TiO₂ layer with the hole-conducting PEDOT and to achieve a good through-space electronic contact between dye molecules and

the hole-conducting materials. We obtained 2.6% of conversion efficiency with high open circuit voltage (~0.8 V) from dye-sensitized solar cells using PEDOT as a hole-conducting material and as a platinum-free counter electrode. There are two processes in polymerization, one is how many PEDOT are made (initiation) and the other is how long they are with distribution (propagation). Quantitatively we could get a numeric value of total polymerization charge and it is hard to assign exactly how many and how long from the current–time curve. The optimum filling of hole-conducting materials is related with both polymerization processes and the pore (pore size and porosity) of nanoporous TiO₂ is important. The effective filling of PEDOT into the dyed mesoscopic TiO₂ electrode is an important factor to achieve the high conversion efficiency.

Acknowledgement

One of authors (Yukyeong Kim) acknowledges the financial support of the Nano System Institute of Seoul National University, Korea.

References

- [1] B. O'Regan, M. Grätzel, Nature 353 (1991) 737–740.
- [2] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Grätzel, Nature 395 (1998) 583–585.
- [3] L. Schmidt-Mende, S.M. Zakeeruddin, M. Grätzel, Appl. Phys. Lett. 86 (2005) 013504.
- [4] H.J. Snath, S.M. Zakeeruddin, L. Schmidt-Mende, C. Klein, M. Grätzel, Angew. Chem. 44 (2005) 6413–6417.
- [5] L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida, M. Grätzel, Adv. Mater. 17 (2005) 813–815.
- [6] L. Schmidt-Mende, M. Grätzel, Thin Solid Films 500 (2006) 296–301.
- [7] K. Murakoshi, R. Kogure, Y. Wada, S. Yanagida, Chem. Lett. 26 (1997) 471–472.
- [8] K. Murakoshi, R. Kogure, Y. Wada, S. Yanagida, Sol. Energy Mater. Sol. Cells 55 (1998) 113–125.
- [9] T. Kitamura, M. Maitani, M. Matsuda, Y. Wada, S. Yanagida, Chem. Lett. 30 (2001) 1054–1055.
- [10] N. Fukuri, Y. Saito, W. Kubo, G.K.R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, J. Electrochem. Soc. 151 (2004) A1745–A1748.
- [11] N. Fukuri, N. Masaki, T. Kitamura, Y. Wada, S. Yanagida, J. Phys. Chem. B 110 (2006) 25251–25258.
- [12] A.J. Mozer, Y. Wada, K.-J. Jiang, N. Masaki, S. Yanagida, S.N. Mori, Appl. Phys. Lett. 89 (2006) 043509.
- [13] Y. Saito, T. Kitamura, Y. Wada, S. Yanagida, Chem. Lett. 31 (2002) 1060–1061.
- [14] Y. Saito, N. Fukuri, G.K.R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, Electrochem. Commun. 6 (2004) 71–74.
- [15] A. Kay, M. Grätzel, J. Phys. Chem. 97 (1993) 6272–6277.
- [16] P. Wang, S.M. Zakeeruddin, R. Humphry-Baker, J.E. Moser, M. Grätzel, Adv. Mater. 15 (2003) 2101–2104.
- [17] P. Wang, S.M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker, M. Grätzel, J. Phys. Chem. B 107 (2003) 14336–14341.
- [18] J. Kruger, R. Plass, L. Cevey, M. Piccirelli, M. Grätzel, U. Bach, Appl. Phys. Lett. 79 (2001) 2085–2087.
- [19] Y. Saito, T. Kitamura, Y. Wada, S. Yanagida, Synth. Met. 131 (2002) 185–187.
- [20] N. Ikeda, K. Teshima, T. Miyasaka, Chem. Commun. (2006) 1733–1735.