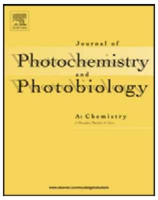
Journal of Photochemistry and Photobiology A: Chemistry 204 (2009) 110–114

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Photoelectrochemical oxidative polymerization of aniline and its application to transparent TiO_2 solar cells

Yukyeong Kim[a,b], Ju-wan Lim[a], Yung-Eun Sung[a,*], Jiang-bin Xia[b],
Naruhiko Masaki[b], Shozo Yanagida[b,**]

[a] *School of Chemical and Biological Engineering, Seoul National University, Sillim-dong, Gwanak-gu, Seoul 151-744, Republic of Korea*
[b] *Center for Advanced Science and Innovation, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan*

ARTICLE INFO

Article history:
Received 13 July 2008
Received in revised form 8 December 2008
Accepted 3 March 2009
Available online 17 March 2009

Keywords:
Quasi-solid-state solar cell
Photoelectrochemical oxidative polymerization

ABSTRACT

Quasi-solid-state transparent TiO_2 solar cells using aniline oligomer as a hole conducting material and PEDOT on FTO as a counter cathode catalyst were newly developed. The pore of the nanoporous TiO_2 layer was filled with aniline oligomer as a hole conductor through the *in situ* photoelectrochemical oxidative polymerization of aniline under photo-excitation of TiO_2 layers. The best efficiency of 0.36% with high open circuit voltage 0.83 V was obtained under simulated 1-sun conditions even though the cells absorb only UV light, containing only 5% photon energy to the total in solar light. The photoelectrochemical synthesis of a conjugated polymer (p-type electron donor) is an effective way to fill the porous structure of inorganic n-type electron acceptor like nanoporous TiO_2 and to obtain the molecular level contact between them.

1. Introduction

Hybrid solar cells are composed of an electron transporting inorganic semiconductor material and a π-conjugated hole conducting organic polymer [1–6]. In the case of metal oxide as an electron transporting materials, these solar cells operate and produce a current in an external circuit by exciton dissociation at the oxide and π-conjugated polymer interface that leads to charge separation and carrier transport through the metal oxide and the hole conducting materials respectively. The charge separation and their transfer at the interface heterojunction is an essential factor in the solar cell performance. Such bulk heterojunction has been realized as a mixture of conductive polymers with fullerene derivatives (PCBM; [6-6]-phenyl C_{61} butyric acid methyl ester) or metal oxide (TiO_2, ZnO) [7–11]. The conducting polymers with extended π-conjugated electron systems such as polypyrrole, polythiophene, polyaniline etc., have shown great promises due to their high absorption coefficients in visible region and high mobility of charge carriers. Many conducting polymers in their undoped (or partially doped) state become electron donors upon photo-excitation and good hole conductors as well [12]. To use these conducting polymers as a light harvesting and hole conductive material, their self-assembled contact with the electron-accepting metal oxide will be indispensable.

The photoelectrochemical synthesis of a conjugated polymer (p-type electron donor) is an effective way to fill the porous structure of inorganic n-type electron acceptor like nanoporous TiO_2 and to obtain the molecular level contact between them [13]. Literature survey revealed the photoelectrochemical formation of polypyrrole or polyaniline as a pattern or an image on TiO_2 films [14,15]. In this study, using photoelectrochemical oxidative polymerization of aniline on the surface of nanoporous TiO_2, transparent TiO_2 solar cells were developed. The photo-excitation of TiO_2 generates holes in the valence band, giving active sites to start oxidative polymerization of aniline, resulting in a very good contact between the nanoporous TiO_2 and the aniline oligomer. Here we introduce a new type of solar cell operated by short-wavelength solar light with verification studies of photoelectrochemical oxidative polymerization of aniline. This solar cell could be categorized as a kind of bulk heterojunction solar cells [16]. However, such cells looked only sensitive to UV light because of very poor absorbance of visible light by aniline oligomer. Recently polyaniline-sensitized TiO_2 solar cells were reported using LiI as hole conductor, giving the conversion efficiency of 1.1% [17]. In addition, the UV photovoltaic cell based on polymer/inorganic bilayer structure was reported with high open-circuit voltage of 1.65 V and the conversion efficiency of 0.11% under low light intensity [18].

2. Experimental details

As for fabrication of TiO_2 photoelectrodes, to avoid electron leakage through a direct electrical contact of fluorine doped tin oxide glass substrate (FTO, NSG 10 ohm/sq) with aniline oligomer as hole

---

[*] Corresponding author. Tel.: +82 2 880 1889; fax: +82 2 888 1604.
[**] Corresponding author. Tel.: +81 6 6879 7351; fax: +81 6 6879 7351.
E-mail addresses: ysung@snu.ac.kr (Y.-E. Sung), yanagida@mls.eng.osaka-u.ac.jp (S. Yanagida).

1010-6030/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2009.03.002

conducting material, a blocking layer composed of compact TiO_2 was introduced onto the FTO with various thickness by spin coating method as reported [19]. The commercially available anatase TiO_2 of Ti-Nanoxide T (Solaronix SA) was used for the photoactive layer of the TiO_2 electrodes. Nanoporous TiO_2 films of 3.5- and 7-μm thickness from once and twice coating, respectively, by doctor-blading were sintered at 450 °C for 30 min. The resulting TiO_2 electrode was immersed into the electrolyte of 0.02 M aniline and 0.5 M H_2SO_4 in aqueous solution for photoelectrochemical oxidative polymerization of aniline. Through the anode side illumination [20] using white light (500 W Xenon lamp) and chronoamperometry using potentiostat (BAS 100B), photoelectrochemical polymerization of aniline was carried out. The effect of various applied voltage and the lapse of time was investigated under fixed light intensity of 250 mW/cm^2. For verification of the systems, electrochemical measurements by cyclic voltammetry, chronoamperometry and photoelectrochemical analysis were carried out using the bare FTO and blocking layered FTO (compact TiO_2 layer) as a working electrode and sulfuric acid aqueous electrolyte with and without the aniline monomer. Platinum wire was used as a counter electrode and Ag/AgCl was used as a reference electrode for all the electrochemical measurements.

The solar cell devices are composed of blocking layered FTO as a transparent conducting substrate, mesoporous TiO_2 as a photoactive layer, aniline oligomer as a hole conducting material and poly(3,4-ethylenedioxythiophene) (PEDOT [21,22]) on FTO as a counter electrode. After *in situ* photoelectrochemical polymerization of aniline, the TiO_2/aniline-oligomer electrode was rinsed using deionized water and dried and then 1 drop of BMIIm (1-butyl-3-methyimidazolium bis-trifluoromethansulfonylamide) with 0.2 M of TBP (t-butylpyridine) and 0.2 M of LiTFSI (lithium bis-trifluoromethanesulfonylamide) was added [23,24]. Using the TiO_2/aniline-oligomer as a photoelectrode and a counter electrode of electrochemically deposited PEDOT on the FTO by chronoamperometry (0.8 V vs. Ag/AgCl, 180 s) as reported [22], a solar cell (active area 0.27 cm^2) was assembled using clips. The photovoltaic performance was measured using simulated light of 100 mW/cm^2 with AM 1.5 filter (Yamashita Denso, YSS-80). The incident photon to current conversion efficiency was obtained using monochromic light of 5 mW/cm^2 (IPCE measurements, PV-25DYE, Jasco).

3. Electrochemical analysis

Polyaniline can be easily synthesized on the conducting substrates by cycle voltammetric, potentiostatic or galvanostatic conditions. Fig. 1 shows cycle-voltammetry of aniline electrodeposition on a FTO. The oxidation of aniline starts at around 1.0 V vs. Ag/AgCl. In our photoelectrochemical method, the oxidation of aniline occurs on the photo-oxidized TiO_2 surface, i.e., holes generated in the valence band by photoexcitation (UV irradiation) of TiO_2 give oxidative polymerization sites. Since the valence band potential of anatase TiO_2 is around 2.5 V vs. Ag/AgCl. The potential of the hole in TiO_2 is high enough to initiate aniline oxidation (Honda-Fujishima-effect [25]). Initiation of oxidation easily occurs but there is no further driving force of propagation to the longer polymer chain. Therefore only oligomer type of aniline polymers was obtained and the color of the resulting film on TiO_2 electrodes was yellow, not green. The obtained film looked very transparent. To confirm that yellow color was an aniline-derived compound, the same photoelectrochemical test using sulfuric acid aqueous electrolyte was carried out in the absence of aniline monomer.

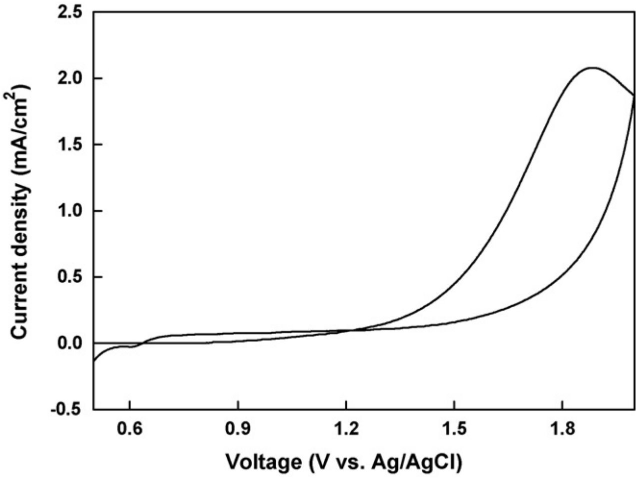


Fig. 1. Cyclic voltammetry of 0.2 M aniline and 0.5 M sulfuric acid aqueous solution. Scan rate is 50 mV/s.

The anatase TiO_2 (band gap is ∼3.2 eV) absorbs UV light generating electron–hole pairs. Without aniline monomer, a redox couple in the electrolyte may be derived by electrolysis of aqueous electrolyte for reduction of holes during the photoelectrochemical reaction, giving high current. On the other hand, in the photoelectrochemical reaction in the co-existence of the aniline monomer, the aniline oxidation starts with protons generation, where SO_4^{2-} acts as a scavenger of proton, leading to aniline oxidation on the TiO_2 surface [26]. The total photoelectrochemical reaction charge is not only related to the aniline oxidation charge but also to the redox reaction of the aqueous electrolyte that does not contribute to reactions with aniline on TiO_2. The current of photoelectrochemical reaction without aniline is found much higher than the one with aniline from the current time curves as shown in Fig. 2. The photoelectrochemical experiments were carried out at 0.2 V vs. Ag/AgCl for 1200 s using sulfuric acid aqueous electrolyte with and without the aniline monomer. The TiO_2 films of 3.5- and 7-μm thickness on the 80-nm thick blocking layered FTO were used as a working electrode. The slightly higher current was obtained from 7-μm thickness TiO_2 compared with 3.5-μm thickness TiO_2 from the photoelectrochemical experiments without aniline and the lower current was obtained from the thicker TiO_2 electrode in the presence of aniline monomer. The slight higher current from the thicker TiO_2 films in the photoelectrochemical experiments in the absence of aniline was noticeable. The current decrease in the presence of aniline is related to selective oxidation of aniline. The nanoporous TiO_2 film with 7-μm thickness has approximately double surface area to the one of 3.5-μm thickness where the successive oxida-

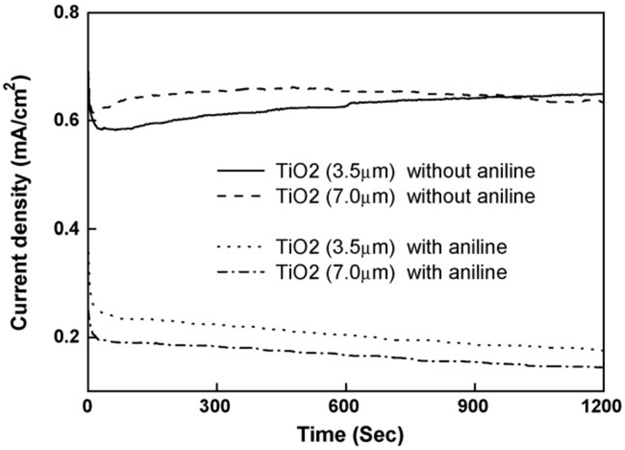


Fig. 2. Current–time curves for photoelectrochemical experiments using porous 3.5- and 7-μm thick TiO_2 films on 80-nm thick blocking-layered FTO in the absence and presence of aniline. Chronoamperometry at 0.2 V vs. Ag/AgCl for 1200 s in aqueous sulfuric acid electrolytes.

tion could occur. The exact charge of aniline oxidation could not be calculated but the current difference from the photoelectrochemical experiments with and without aniline might be connected with rather slow oxidative polymerization of aniline on TiO_2.

4. Application to the solar cells

Photoelectrochemical polymerization of aniline was carried out by potentiostatic method under various applied potentials and reaction time. The compact TiO_2 films as a blocking layer is designed for prohibiting electron leakage at nanoporous TiO_2 films and FTO as reported for dye-sensitized TiO_2 solar cells. The blocking layered FTOs with 50-, 80-, 130-nm thicknesses of compact TiO_2 layer were prepared by spin coating method. Nanoporous TiO_2 films with 7-μm thickness on the bare and blocking layered FTOs were used as a working electrode for photoelectrochemical oxidation reaction. Fig. 3 shows electrochemical polymerization curves of aniline on bare FTO and blocking layered FTOs (50-, 80-, 130-nm thick TiO_2 compact layer) by potentiostatic conditions of 1.5 V vs. Ag/AgCl for 1500 s. The electrical oxidation of aniline occurs very smoothly on FTO but not on the TiO_2-blocked FTO. This fact can be rationalized that there will be a high sheet resistance between bare FTO and blocking layered TiO_2 layer under dark conditions.

Fig. 4 shows current time curves of photoelectrochemical oxidative polymerization of aniline under UV light irradiation on TiO_2 films on FTO (TiO_2/FTO) electrodes. Interestingly, the current increased with increasing the blocking TiO_2 layer thickness of the TiO_2/FTO electrodes, which is quite contrast to the electrochemical oxidative polymerization of aniline on this compact layered FTO (Fig. 3). Fig. 5 shows the photoelectrochemical experiments in the absence of aniline that can be regarded as a kind of Honda-Fujishima effect experiments [25]. The presence of either blocking layer or nanoporous layer of TiO_2 showed photocurrent under chronoamperometry at 0.2 V vs. Ag/AgCl. The highest current in the case of the nanoporous TiO_2 electrode on the 80-nm thick TiO_2 blocking layered FTO indicates that electron–hole pairs could be generated not only from nanoporous TiO_2 layer but also from the TiO_2 compact layer itself through the band-gap excitation of the TiO_2/FTO electrodes. This interpretation explains the current difference in Fig. 4 (higher current from thicker blocking layered FTO) as due to the concurrent generation of electron–hole pairs in TiO_2 compact layer.

Fig. 6 shows photovoltaic *I–V* curves from the assembled solar cells using aniline oligomer doped 7-μm thick TiO_2 films onto the various thick blocking-layered FTOs. High open circuit volt-

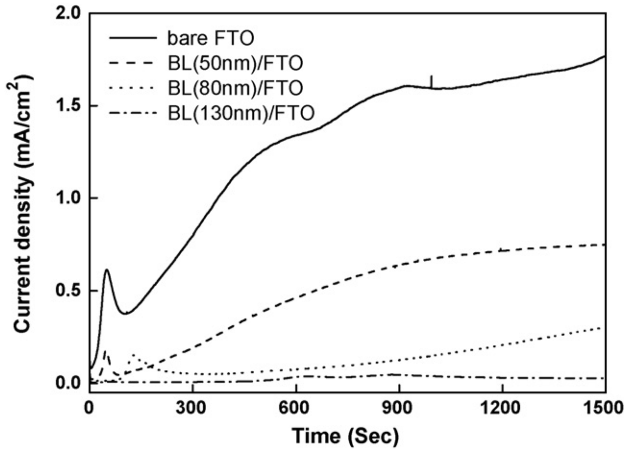


Fig. 3. Electrodeposition curves of 0.2 M aniline and 0.5 M sulfuric acid aqueous solution on the bare FTO and the blocking-layered (BL) FTOs with 50-, 80-, 130-nm thick TiO_2 compact layer. Chronoamperometry at 1.5 V vs. Ag/AgCl for 1500 s.

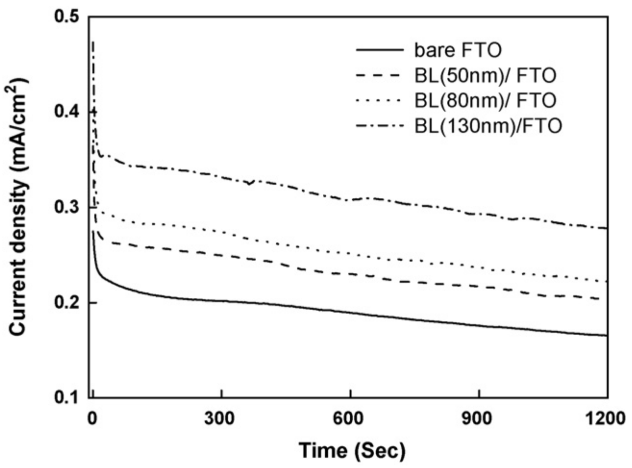


Fig. 4. Current–time curves of photoelectrochemical oxidative polymerization of aniline on the 7-μm thick porous TiO_2 films prepared on various blocking-layered (BL) FTOs; bare FTO and 50-, 80-, 130-nm thick blocking-layered FTOs. Chronoamperometry at 0.2 V vs. Ag/AgCl for 1200 s.

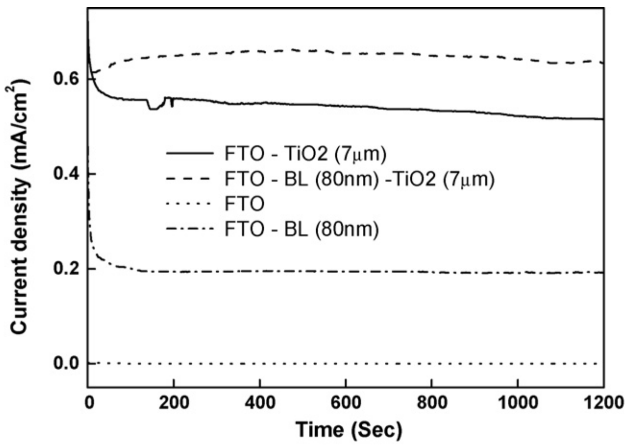


Fig. 5. Photoelectrochemical current curves of 7-μm thick porous TiO_2 films on the bare FTO and 80-nm thick blocking-layered FTO; including the results of same experiments using bare FTO and 80-nm thick blocking-layered FTO. Chronoamperometry at 0.2 V vs. Ag/AgCl for 1200 s in 0.5 M sulfuric acid aqueous electrolytes (absence of aniline).

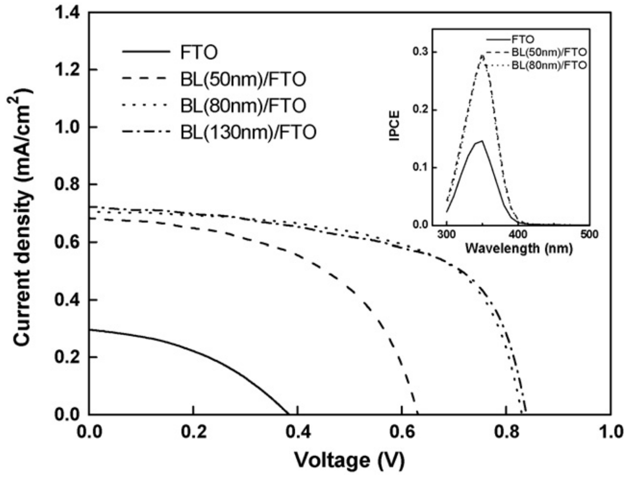


Fig. 6. Effect of compact TiO_2 blocking layer on *I–V* curves of the assembled solar cells. TiO_2/aniline-oligomer photoelectrodes with 7-μm thickness on the blocking layered FTOs; bare FTO and 50-, 80- and 130-nm thick blocking-layered FTOs. IPCE curves obtained after *I–V* measurements shown as inset.

age (Voc, ~0.80 V) and short circuit photocurrent density (Jsc, ~0.70 mA/cm^2) could be achieved when more than 80-nm thick blocking layered FTO was introduced to the photoelectrodes. In the case of the assembled cell using 80-nm thick TiO_2 compact layer between FTO and nanoporous TiO_2 film as a hole blocking layer, Voc of 0.84 V, Jsc of 0.72 mA/cm^2, fill factor of 0.60 and solar energy to electricity conversion efficiency of 0.36% was achieved. The assembled solar cell not introduced hole blocking layer in TiO_2 photoelectrode, shows the conversion efficiency of 0.05% with low Voc of 0.38 V. The aniline oligomer should work as a hole conductor through their molecular level self-assembling and electronic communication on nanoporous and blocking layers of TiO_2. Inset of Fig. 6 shows incident photon-to-electron conversion efficiency (IPCE) curves of the cells at the maximum at around $\lambda = 350$ nm, revealing that the photochemical cells are operated under UV light not by photo-excitation of hole conductive aniline oligomer. The highest value of 0.36% conversion efficiency was again confirmed by obtaining short circuit current of 0.71 mA/cm^2 and open circuit voltage of 0.83 V and fill factor of 0.62 under simulated 1-sun conditions.

Secondly, we examined effects of the applied potentials (0.2, 1.5, 2.5 V vs. Ag/AgCl) on photoelectrochemical oxidation of aniline to verify the photo-electrode system. The applied potential of 1.5 V vs. Ag/AgCl is high enough to oxidize aniline electrochemically, and that of 2.5 V vs. Ag/AgCl is almost the same position of TiO_2 valence band potential. Nanoporous TiO_2 electrodes with 3.5-μm thickness on the 80-nm thick TiO_2 blocking layered FTO were used as working electrodes. Fig. 7 shows the current–time curves of the photoelectrochemical oxidative polymerization of aniline under various applied potentials under UV light irradiation. The higher current was obtained from higher applied potential, though the difference was not so large between the applied potentials of 1.5 and 0.2 V vs. Ag/AgCl. Since the electric field affects the migration of redox couples, the high electric field could increase photoelectrochemical oxidation of not only the migrating aniline but also the redox couples from aqueous sulfuric acid electrolytes on the TiO_2 electrodes.

On the other hand, the same experiments carried out using UV-cut filter (under irradiation of $\lambda \geq 500$ nm) as exemplified by the applied potential of 0.2 V vs. Ag/AgCl shown in Fig. 7, no photocurrent was observed. The electrochemical polymerization (electrodeposition) of aniline was not observed on the TiO_2 electrodes even at the high applied potential of 1.5 and 2.5 V vs. Ag/AgCl, and only yellow colored films were obtained when photoelectrochemical oxidation of aniline was carried. The photochemical oxidation of aniline was relatively slow at the positive potential created by outer electric field. These facts verify that UV light excitation of TiO_2 is essential for *in situ* photoelectrochemical oxidative polymerization of aniline, dominating the formation of aniline oligomer in the vicinity of the nanoporous TiO_2 layers.

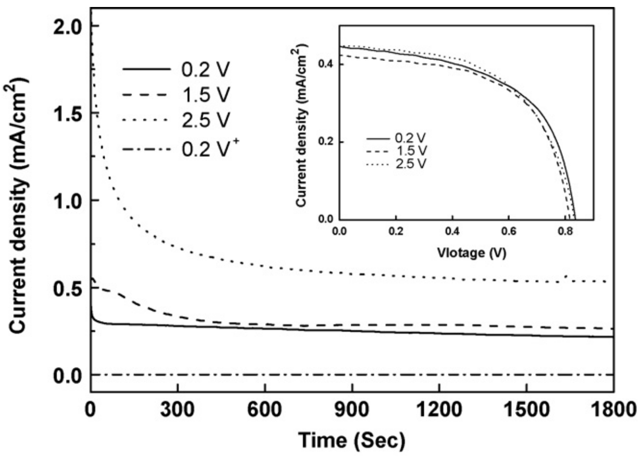


Fig. 7. (a) Current–time curves of photoelectrochemical oxidative polymerization of aniline on the 3.5-μm thick TiO_2 films onto 80-nm thick blocking-layered FTO. Chronoamperometry at various applied potentials of 0.2, 1.5 and 2.5 V vs. Ag/AgCl for 1800 s (0.2 V$^+$; 0.2 V vs. Ag/AgCl using UV-cut filter). Inset shows the effect of applied potentials on *I–V* curves of the assembled solar cells.

The inset in Fig. 7 shows the *I–V* curves of the assembled cells using the resulting TiO_2/aniline oligomer electrodes and PEDOT counter electrodes. Interestingly, there is no large difference in the photovoltaic performance among the electrodes. The observation of high current density at 2.5 V vs. Ag/AgCl in Fig. 7 suggests that this came from the concurrent redox reaction of aqueous electrolytes on the electrodes. Anyhow, the applied potential for the TiO_2/aniline oligomer electrodes ranged broadly from 0.1 to 2.5 V vs. Ag/AgCl, and we could obtain the high conversion efficiency of 0.26% with Jsc = 0.53 mA/cm^2 with 3.5-μm thickness nanoporous TiO_2 electrode under simulated 1-sun conditions.

5. Conclusions

A transparent TiO_2 solar cell was developed by assembling the aniline oligomer infiltrated nanoporous TiO_2 electrodes as photoanodes and PEDOT/FTO electrode as a counter photo-cathode. The aniline oligomer infiltrated TiO_2 electrodes were successfully prepared by the *in situ* photoelectrochemical oxidative polymerization of aniline using nanoporous TiO_2 films on the compact TiO_2 blocking layered FTOs. IPCE curves are consistent with the absorption of TiO_2, suggesting that the solar cells can work under UV light excitation of TiO_2. The maximum conversion efficiency 0.36% was obtained with respectable open circuit voltage of 0.83 V and fill factor of 0.62 under simulated 1-sun conditions. The *in situ* photoelectrochemical infiltration of aniline oligomer may give an electronic contact between nanoporous TiO_2 and hole-conducting aniline oligomer. The light-to-electron conversion efficiency is not high enough even when taken into consideration that the photon energy below $\lambda = 400$ nm is ~5% of the total solar photon energy. However, the new bulk heterojunction-type transparent solar cells, in other words, Honda-Fujishima-effect solar cells could be applied to energy-producing UV-blocking windows in future.

References

[1] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Adv. Funct. Mater. 11 (2001) 15.
[2] H. Spanggaard, F.C. Krebs, Solar Energy Mater. Solar Cells 83 (2004) 125.
[3] K.M. Coakley, M.D. McGehee, Chem. Mater. 16 (2004) 4533.
[4] H. Hoppe, N.S. Sariciftci, J. Mater. Res. 19 (2004) 1924.
[5] J.-D. Kwon, P.-H. Kim, J.-H. Keum, J.S. Kim, Solar Energy Mater. Solar Cells 83 (2004) 311–321.
[6] R.A.J. Janssen, J.C. Hummelen, N.S. Sariciftci, MRS Bull. 30 (2005) 33.
[7] C.Y. Kwong, W.C.H. Choy, A.B. Djurisic, P.C. Chui, K.W. Cheng, W.K. Chan, Nanotechnology 15 (2004) 1156.
[8] W.J.E. Beek, M.M. Wienk, R.A.J. Janssen, Adv. Mater. 16 (2004) 1009.
[9] D.C. Olson, J. Piris, R.T. Collins, S.E. Shabeen, D.S. Ginley, Thin Solid Films 496 (2006) 26.
[10] M. Lira-Cantu, K. Norrman, J.W. Andreasen, F.C. Krebs, Chem. Mater. 18 (2006) 5684.
[11] G.K.R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, J. Photochem. Photobiol. A: Chem. 164 (2004) 61.
[12] S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, J.C. Hummelen, Appl. Phys. Lett. 78 (2001) 841.
[13] K. Murakoshi, R. Kogure, Y. Wada, S. Yanagida, Chem. Lett. 26 (1997) 471.
[14] H. Yoneyama, N. Takahashi, S. Kuwabata, J. Chem. Soc., Chem. Commun. (1992) 716.
[15] M. Okano, K. Itoh, A. Fujishima, J. Electrochem. Soc. 134 (1987) 837.
[16] Z. Liu, J. Zhuo, H. Xue, L. Shen, H. Zang, W. Chen, Synthetic Met. 156 (2006) 721.
[17] S. Tan, J. Zhai, M. Wan, Q. Meng, Y. Li, L. Jiang, D. Zhu, J. Phys. Chem. B 108 (2004) 18693.
[18] H. Jin, Y. How, X. Meng, F. Teng, Chem. Phys. 330 (2006) 501.
[19] Y. Saito, N. Fukuri, R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, Electrochem. Commun. 6 (2004) 71.
[20] N. Fukuri, N. Masaki, T. Kitamura, Y. Wada, S. Yanagida, J. Phys. Chem. B 110 (2006) 25251.

[21] J. Xia, N. Masaki, K. Jiang, S. Yanagida, J. Mater. Chem. 17 (2007) 2845.
[22] Y. Kim, Y.-E. Sung, J. Xia, M. Lira-Cantu, N. Masaki, S. Yanagida, J. Photochem. Photobiol. A: Chem. 193 (2008) 77.
[23] Y. Saito, T. Kitamura, Y. Wada, S. Yanagida, Synthetic Met. 131 (2002) 185.
[24] J. Kruger, R. Plass, L. Cevey, M. Piccirelli, M. Gratzel, U. Bach, Appl. Phys. Lett. 79 (2001) 2085.
[25] A. Fujishima, K. Honda, Nature 238 (1972) 38.
[26] R. Murugesan, E. Subramanian, Mater. Chem. Phys. 80 (2003) 731.