Organic Electronics 13 (2012) 514–518

Contents lists available at SciVerse ScienceDirect

Organic Electronics

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

Highly efficient all solid state dye-sensitized solar cells by the specific interaction of CuI with NCS groups II. Enhancement of the photovoltaic characteristics

Hitoshi Sakamoto [*], Sho Igarashi, Mariko Uchida, Kazuma Niume, Masayuki Nagai

Department of Energy Science and Nuclear Engineering, Energy Materials Chemistry Laboratory, Advanced Research Laboratory,
Tokyo City University, 8-15-1 Todoroki, Setagaya-ku, Tokyo 158-0082, Japan

ARTICLE INFO

Article history:
Received 12 October 2011
Received in revised form 10 November 2011
Accepted 19 November 2011
Available online 21 December 2011

Keywords:
All solid state dye-sensitized solar cells
Interface
Specific interaction
Counter electrode with large surface area
CuI
PEDOT:PSS

ABSTRACT

Highly efficient all solid state dye-sensitized solar cells (DSSC) were fabricated by the specific interaction of CuI with the NCS groups of the dye molecules and that of the counter electrodes. The counter electrodes were prepared by blending nano size carbon in the PEDOT:PSS dispersion. The counter electrodes were covered with the solution containing guanidine thiocyanate, and heated to give the electrode with larger number of NCS groups. Electrostatic adsorption between PEDOT:PSS and guanidine was investigated by X-ray photoelectron spectroscopy (XPS). DSSC were prepared by connecting the NCS groups of the dye molecule with those of the counter electrode with large surface area. The performances of the resulting DSSC were improved dramatically by the increase of the NCS groups on the counter electrode. It is noteworthy that the performances of the cell were higher than that of the cells prepared by the conventional liquid electrolyte. The highly efficient all solid state DSSC are manufactured with inexpensive and low quality materials, and the practical use is promising.

1. Introduction

Dye-sensitized solar cells have been intensively studied as a possible next generation solar cell owing to their simple structure, inexpensive fabrication process and relatively high energy conversion efficiency [1,2]. Unfortunately, the liquid electrolyte presents several technological problems such as dye desorption, solvent evaporation and the leakage of the volatile solvents. Therefore, many efforts were made to replace the liquid electrolyte with solid type hole transporting materials [3–23]. Of the hole conductors obtained, the highest energy conversion efficiency has been obtained with CuI [14–21]. However, the CuI based all solid state dye-sensitized solar cells (DSSC) underwent rapid decay. It is clear that forming a direct contact to such an uneven film using a rigid CuI is very difficult, giving only a few points contact, which is manifested in the unstable and the low energy conversion efficiency of the resulting DSSC. Consequently, counter electrode containing NCS groups were prepared and connected with NCS groups of the dye molecule by CuI to give the stable DSSC in our last study [24].

In the present study, counter electrodes with larger surface area were prepared by blending nano size carbon in the PEDOT:PSS dispersion. The counter electrodes were covered with the solution containing guanidine thiocyanate, and heated to give the electrode with NCS groups. DSSC were prepared by connecting the NCS groups of the dye molecules with those of the counter electrode with larger surface area. The performance of the resulting DSSC was improved dramatically. The improvement is due to the increase of NCS groups on the counter electrode, which is connected with those of dye molecules by CuI. It is noteworthy that the performances of the cell were higher than that of the cells prepared by the conventional liquid

---

[*] Corresponding author.
E-mail address: g0991903@tcu.ac.jp (H. Sakamoto).

1566-1199/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.orgel.2011.11.017

electrolyte. The highly efficient all solid state DSSC are manufactured with inexpensive and low quality materials, and the practical use is promising.

2. Experimental

A compact TiO_2 layer was deposited onto FTO (AGC type U TCO glass) by spray pyrolysis. The TiO_2 paste was prepared [25] and coated onto the FTO using squeeze printing technique (film area = 0.5 cm^2), and then the electrode was heated at 450 °C for 30 min in air. The post-treatment with $TiCl_4$ aqueous solution was applied to the prepared films by soaking in 0.2 M aqueous $TiCl_4$ at 70 °C for 30 min, followed by a water rinse and fired at 450 °C for 30 min. The thickness of porous TiO_2 film was about 7 μm. The porous TiO_2 film was immersed into 0.5 mM ethanol solution of N3 dye (Kojima Chemicals Co.) for 12 h at room temperature. The coating of CuI onto dyed electrodes was performed in N_2-atmosphere in a glove box. The CuI-acetonitrile solution (0.15 M) was lightly coated over the dyed electrode. After coating, the electrode was heated to 80 °C to evaporate the solvent. This process was repeated several times. The counter electrode was prepared by coating the solution containing guanidine thiocyanate onto the TCO glass modified by PEDOT layer. The solution containing guanidine was prepared by dissolving PEG20000 and guanidium thiocyante (1:1) in acetonitrile. The PEDOT modified TCO glass was prepared by spin coating of PEDOT:PSS aqueous dispersion (Clevios PH) on TCO glass and dried at 100 °C for 30 min in vacuum. In order to increase the surface area of counter electrode, carbon blacks (Strem Chemicals) (30, 100, 200 or 300 wt.% with respect to the PEDOT:PSS) is added to PEDOT:PSS aqueous dispersion. The CuI/dye/TiO_2 glass plate was fixed together with the counter electrode. The resulting cells had an active area of 0.25 cm^2.

X-ray photoelectron spectroscopy (XPS) measurement was performed using SSX-100 instrument using a monochromatized Al Kα X-rays at $h\nu$ = 1487 eV. AFM analysis was performed with a SPA400 (Seiko Instruments Inc.) using the tapping mode. The photoelectrochemical properties of the DSSC were studied by recording the current–voltage (I–V) characteristics under illumination of AM1.5 (1 Sun; 100 mW/cm^2) by using a solar simulator (Yamashita Denso). The electrochemical impedance spectroscopy (EIS) of the DSSC was measured with an impedance analyzer (Solartron Analytical, 1260) connected with a potentiostat (Solartron Analytical, 1287) under illumination of AM1.5 by using a solar simulator. The EIS was recorded over frequency range of 0.1–10^6 Hz. The AC amplitude and the applied voltage were 10 mV and set at Voc of the cells, respectively.

3. Results and discussion

3.1. Electrostatic adsorption between PEDOT:PSS and guanidine

In order to analyze the electrostatic adsorption between PEDOT:PSS and guanidine qualitatively, S element was investigated with XPS technique, and the result is shown in Fig. 1. The S 2p core level shows large differences in binding energy depending on the S location (PEDOT or PSS). Low binding energy peak corresponds to PEDOT and high binding energy peak comes from PSS. In PEDOT:PSS mixed with guanidine hydrochloride (1:0.6) sample, the peak originating from PSS shifted to higher binding energy position. This change is similar to electrostatic adsorption between PEDOT:PSS and Octadecylamine [26]. This shift shows the formation of electrostatic force of PSS and ionization of guanidine changes S chemical environment in PSS, which results in the S 2p binding energy shifts to higher position.

3.2. Fabrication of highly efficient all solid state DSSC

Fig. 2 shows AFM images of PEDOT:PSS films coated on TCO glasses. The PEDOT:PSS film on ITO glass was flat (Fig. 2a). The PEDOT:PSS film on FTO glass was somewhat rougher because of FTO glass with some textures (Fig. 2b). Counter electrodes with larger surface area were prepared by adding nano size carbon (avg. particle size: 42 nm) in the PEDOT:PSS dispersion (Fig. 3). The counter electrodes were covered by the solution containing guanidine thiocyanate on this film and a series of counter electrodes containing NCS groups were prepared. Highly efficient all solid state DSSC have been prepared by connecting the NCS groups with those of counter electrode by CuI.

3.3. Photovoltaic performance of the all solid state DSSC

Fig. 4 shows the photocurrent–voltage characteristics of the all solid state DSSC with the series of counter electrodes. The properties of the DSSC were summarized in Table 1. The properties were improved dramatically by blending nano size carbon in the PEDOT:PSS dispersion. The conversion efficiency was improved from 2.9% to 7.4%. In our latest study, the DSSC with PEDOT:PSS on FTO showed conversion efficiency of 4.2% [24]. Surface area of PEDOT:PSS film on FTO glass was larger than that of the film on ITO glass, as shown in Fig. 2. The counter electrodes were covered by the solution containing guanidine thiocyanate on this film. The photovoltaic performance was improved by using the counter electrode with larger surface area.

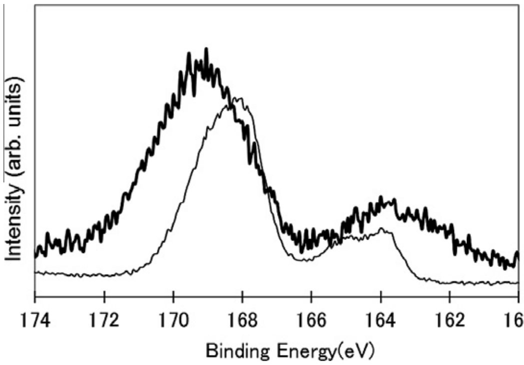

Fig. 1. S 2p core level spectra of PEDOT:PSS (solid curve) and guanidine + PEDOT:PSS (bold curve).

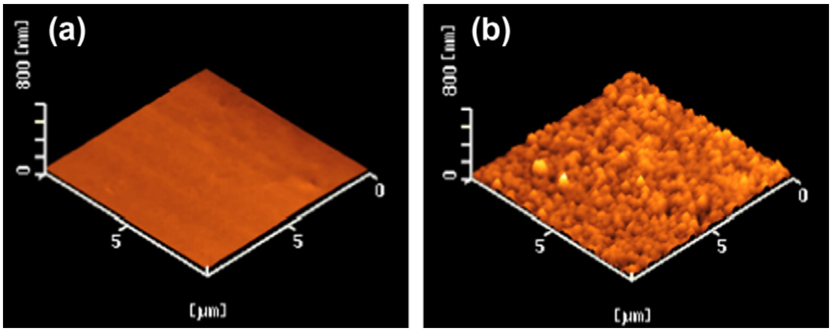

Fig. 2. AFM images of PEDOT:PSS coated on TCO glasses. (a) PEDOT:PSS on ITO glass; (b) PEDOT:PSS on FTO glass.

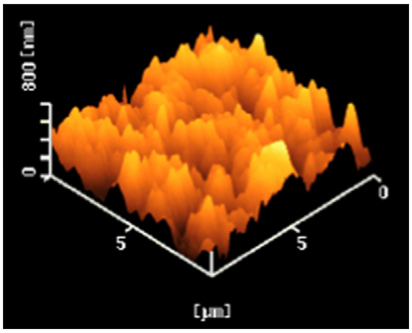

Fig. 3. AFM images of PEDOT:PSS (C: 200 wt.%) coated on ITO glasses.

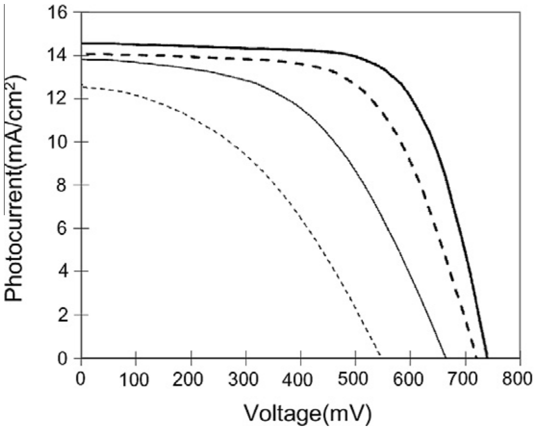

Fig. 4. Photocurrent-voltaic curves of all solid state DSSC fabricated from different counter electrode: PEDOT:PSS (dash curve), PEDOT:PSS (C: 30 wt.%) (solid curve), PEDOT:PSS(C: 100 wt.%)(bold-dash curve), PEDOT:PSS(C: 200 wt.%) (bold curve).

Table 1
Comparison of the performance of the all solid state DSSC.

Counter electrode	J_{sc} (mAcm^{-2})	V_{oc} (mV)	FF	η (%)
PEDOT:PSS	12.5	546	0.42	2.86
PEDOT:PSS(C: 30 wt.%)	13.8	664	0.51	4.68
PEDOT:PSS(C: 100 wt.%)	14.0	720	0.63	6.36
PEDOT:PSS(C: 200 wt.%)	14.5	739	0.69	7.40
PEDOT:PSS(C: 300 wt.%)	14.4	725	0.68	7.05

In order to study the large improvement of the performance of the DSSC containing nano size carbon, the charge transfer resistance of the three dominant interfaces were investigated by electrochemical impedance spectroscopy. Fig. 5 shows Nyquist plots recorded over frequency range of 0.1–10^6 Hz of all solid state DSSC used different carbon contents under open circuit conditions. According to previous studies [24], the equivalent circuit of DSSC can be shown as the inset in Fig. 5a. Fig. 5b is the enlarged part of high frequencies in the Nyquist plots. We assumed that R_1C_1, R_2C_2 and R_3C_3 correspond to a charge-transfer resistance and an electrochemical capacitance formed by TiO_2·dye/CuI, CuI/guanidine thiocyanate and guanidine thiocyanate/PEDOT:PSS interface, respectively. R_0 indicates the series resistance of the DSSC. Those values of R, C and α were obtained by fitting with Z-view software shown in Table 2.

In Fig. 4, I can see that the higher cell performance is attributing to the lower resistance within the cell. In Table 2, R_3 was reduced drastically with a carbon content in PEDOT:PSS, corresponding to the interface resistance between guanidine thiocyanate/PEDOT:PSS was largely decreased, which seems to be the factor that reduced the total resistivity within the cell to attain a higher cell performance. Lower electrical resistance of PEDOT:PSS with carbon is the reason for the higher cell performance. The improvement is also due to the increase of the number of NCS groups on the counter electrode with larger surface area, which is connected with those of dye molecules by CuI.

4. Conclusion

An efficient all solid state dye-sensitized solar cells have been prepared by the specific interaction of CuI with the NCS groups of the dye molecules and the NCS groups of the counter electrode. The counter electrode were prepared by coating the solution containing guanidine thiocyanate on PEDOT:PSS modified FTO. The resulting all solid state DSSC were stable, and exhibited relatively high conversion efficiency.

In the present study, the electrostatic adsorption between PEDOT:PSS and guanidine was investigated by XPS (Fig. 1), and the performance of DSSC was improved by using counter electrodes with larger surface area. The counter electrodes with larger surface area were prepared by blending nano size carbon in the PEDOT:PSS dispersion. The film

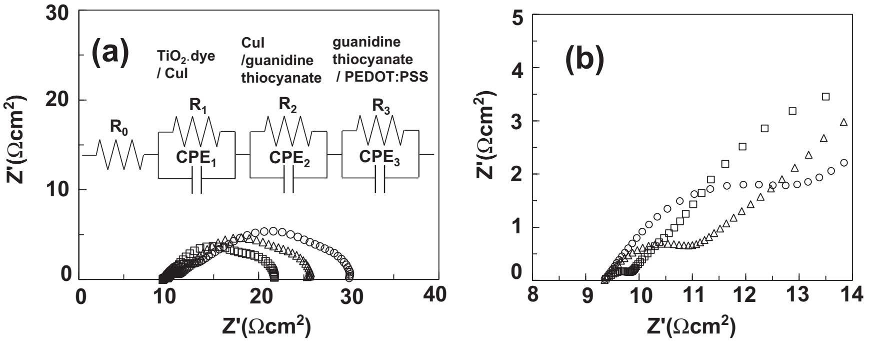

Fig. 5. Impedance spectra obtained under illumination for the cell with EDOT:PSS(○), PEDOT:PSS blending carbon particles (C: 30wt.%(Δ), 200wt.%(□)).

Table 2
Parameters obtained by fitting the impedance spectra of DSSC with PEDOT:PSS and PEDOT:PSS blending carbon particles, using the equivalent circuit (Fig. 5a).

	R_0 (Ωcm^2)	R_1 (Ωcm^2)	C_1 (Fcm^{-2})	α	R_2 (Ωcm^2)	C_2 (Fcm^{-2})	α	R_3 (Ωcm^2)	C_3 (Fcm^{-2})	α
PEDOT:PSS	9.28	2.94	1.6×10^{-2}	1	13.3	1.1×10^{-3}	0.80	4.67	1.7×10^{-4}	0.71
PEDOT:PSS (C: 30 wt.%)	9.34	3.07	2.0×10^{-2}	1	11.4	1.5×10^{-3}	0.80	2.10	1.7×10^{-4}	0.71
PEDOT:PSS (C: 200 wt.%)	9.44	3.00	2.2×10^{-2}	1	8.95	2.3×10^{-3}	0.78	0.47	3.8×10^{-4}	0.70

morphology was shown in Fig. 3. The counter electrodes were covered by the solution containing guanidine thiocyanate, and heated to give the electrodes with larger number of NCS groups. The DSSC were investigated by electrochemical impedance spectroscopy, and those value of R_2 and R_3 were decreased by adding nano size carbon (C: 200 wt.%). The resulting all solid state DSSC exhibited dramatically high conversion efficiency (7.4%). The improvement is due to the increase of the NCS groups on the counter electrode, which resulted in the DSSC with high conversion efficiency. It is noteworthy that the performances of the cell were higher than that of the cells prepared by the conventional liquid electrolyte. The all solid state dye-sensitized solar cells are manufactured with inexpensive and low quality materials, and the practical use is promising.

References

[1] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films, Nature (Lond) 353 (1991) 737–740.
[2] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humohry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, Conversion of light to electricity by cis-X2Bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X=Cl$^-$, Br$^-$, I$^-$, CN$^-$, and SCN$^-$) on Nanocrystalline TiO_2 Electrodes, J. Am. Chem. Soc. 115 (1993) 6382–6390.
[3] M. Matsumoto, H. Miyazaki, K. Matsuhiro, Y. Kumashiro, Y. Takaoka, A dye sensitized TiO_2 photoelectrochemical cell constructed with polymer solid electrolyte, Solid State Ionics 89 (1996) 263–267.
[4] K. Murakoshi, R. Kogure, Y. Wada, S. Yanagida, Solid State Dye-Sensitized TiO_2 Solar Cell with Polypyrrole as Hole Transport Layer, Chem. Lett. 26 (1997) 471–472.
[5] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissörtel, J. Salbeck, H. Speitzer, M. Grätzel, Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies, Nature 395 (1998) 583–585.
[6] J. Krüger, R. Plass, L. Cevey, M. Piccirelli, M. Grätzel, High efficiency solid-state photovoltaic device due to inhibition of interface charge recombination, Appl. Phys. Lett. 79 (2001) 2085–2087.
[7] J. Bandara, H. Weerasinghe, Solid-state dye-sensitized solar cell with p-type NiO as a hole collector, Sol. Energy Mater. Sol. Cells 85 (2005) 385–390.
[8] N. Fukuri, N. Masaki, T. Kitamura, Y. Wada, S. Yanagida, Electron transport analysis for improvement of solid-state dye-sensitized solar cells using poly(3,4-ethylenedioxythiophene) as hole conductors, J. Phys. Chem. B 110 (2006) 25251–25258.
[9] J. Xia, N. Masaki, M. Lira-Cantu, Y. Kim, K. Jiang, S. Yanagida, Influence of doped anions on poly(3,4-ethylenedioxythiophene) as hole conductors for iodine-free solid-state dye-sensitized solar cells, J. Am. Chem. Soc. 130 (2008) 1258–1263.
[10] B. O' Regan, D.T. Schwartz, Efficient dye-sensitized charge separation in a wide-band-gap p-n heterojunction, J. Appl. Phys. 80 (1996) 4749–4754.
[11] B. O'Regan, D.T. Schwartz, S.M. Zakeeruddin, M. Grätzel, Electrodeposited nanocomposite n–p heterojunctions for solid-state dye-sensitized photovoltaics, Adv. Mater. 12 (2000) 1263–1267.
[12] G.R.R.A. Kumara, A. Konno, G.K.R. Senadeera, P.V.V. Jayaweera, D.B.R.A. De Silva, K. Tennakone, Dye-sensitized solar cell with the hole collector p-CuSCN deposited from a solution in *n*-propyl sulphide, Sol. Energy Mater. Sol. Cells 69 (2001) 195–199.
[13] M.K.I. Senevirathna, P.K.D.D.P. Pitigala, V.P.S. Perera, K. Tennakone, Langmuir 21 (2005) 2997–3001.
[14] K. Tennakone, G.R.R.A. Kumara, A.R. Kumarasinghe, K.G.U. Wijayantha, P.M. Sirimanne, A dye-sensitized nano-porous solid-state photovoltaic cell, Semicond. Sci. Technol. 10 (1995) 1689–1693.
[15] K. Tennakone, G.R.R.A. Kumara, I.R.M. Kottegoda, K.G.U. Wijayantha, V.P.S. Perera, A solid-state photovoltaic cell sensitized with a ruthenium bipyridyl complex, J. Phys. D.: Appl. Phys. 31 (1998) 1492–1496.
[16] K. Tennakone, V.P.S. Perera, I.R.M. Kottegota, L.A.A. De Silva, G.R.R.A. Kumara, A. Konno, Dye-sensitized solid-state photovoltaic cells: Suppression of electron-hole recombination by deposition of the dye on a thin insulating film in contact with a semiconductor, J. Electron. Mater. 30 (2001) 992–996.
[17] G.R.R.A. Kumara, A. Konno, K. Shiratychi, J. Tukahara, K. Tennakone, Dye-sensitized solid-state solar cells: use of crystal growth inhibitors for deposition of the hole collector, Chem. Mater. 14 (2002) 954–955.
[18] P.M. Sirimanne, T. Jeranko, P. Bogdanoff, S. Fiechter, H. Tributsch, On the photo-degradation of dye sensitized solid-state TiO_2 |dye|CuI cells, Semicond. Sci. Technol. 18 (2003) 708–712.

[19] Q.-B. Meng, K. Takahashi, X.-T. Zhang, I. Sutanto, T.N. Rao, O. Sato, A. Fujishima, H. Watanabe, T. Nakamori, M. Uragami, Fabrication of an efficient solid-state dye-sensitized solar cell, Langmuir 19 (2003) 3572–3574.

[20] V.P.S. Perera, K. Tennakone, Recombination processes in dye-sensitized solid-state solar cells with CuI as the hole collector, Sol. Energy Mater. Sol. Cells 79 (2003) 249–255.

[21] X.-T. Zhang, H.-W. Liu, T. Taguchi, Q.-B. Meng, O. Sato, A. Fujishima, Slow interfacial charge recombination in solid-state dye-sensitized solar cell using Al_2 O_3-coated nanoporous TiO_2 films, Sol. Energy Mater. Sol. Cells 81 (2004) 197–203.

[22] A. Fujishima, X.-T. Zhang, Solid-state dye-sensitized solar cells, Proc. Japan Acad. 81 (B) (2005) 33–42.

[23] A.J. Mozer, D.K. Panda, S. Gambhir, T.C. Romeo, B.W. Jensen, G.G. Wallace, Flexible and compressible Goretex−PEDOT membrane electrodes for solid-state dye-sensitized solar cells, Langmuir 26 (2010) 1452–1455.

[24] P.G. Karlsson, S. Bolik, J.H. Richter, Interfacial properties of the nanostructured dye-sensitized solid heterojunction $TiO_2/RuL_2(NCS)_2$ /CuI, J. Chem. Phys. 120 (2004) 11224–11232.

[25] H. Sakamoto, S. Igarashi, K. Niume, M. Nagai, Highly efficient all solid state dye-sensitized solar cells by the specific interaction of CuI with NCS groups, Org. electron. 12 (2011) 1247–1252.

[26] U.O. Krašovec, M. Bergic, M. Hočevar, M. Topič, Unique TiO_2 paste for high efficiency dye-sensitized solar cells, Sol. Energy Mater. Sol. Cells 93 (2009) 379–381.