Improvement of photovoltaic performance of solid-state dye-sensitized solar cells by iodine doping in conjugated polymer

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Abstract

The performance of solid-state dye-sensitized solar cells using a conjugated polymer, poly(2-methoxy,5-(2′-ethyl-hexoxy)-1,4-phenylenevinylene) (MEHPPV), was greatly improved by iodine doping in the hole transporting layer. The surface photovoltage spectroscopy (SPS) and electric-field-induced surface photovoltage spectroscopy (EFISPS) study on the undoped and iodine doped MEHPPV films were performed and indicated that iodine doping turned the n-type conduction of MEHPPV to p-type conduction, which was accompanied by an improvement of photocurrent from $27 \, \mu A/cm^2$ to $148 \, \mu A/cm^2$.
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1. Introduction

In the last decade, dye-sensitized solar cells (DSSCs) have been developed into one of the most interesting alternatives to current solar cell technology [1,2]. Although the devices based on liquid electrolyte have reached the efficiency as high as 10% under AM 1.5 $(1000 \, W/m^2)$ [3], the main problem that the liquid electrolyte may limit the device stability still remains. Recently, researches on the replacement of liquid electrolyte by solid or quasi-solid state hole transporters such as polymer electrolyte [4], room temperature molten salt [5], inorganic semiconductor [6], have been reported. Meanwhile, much attention has also been paid to employing organic hole transporter in all solid-state solar cells which possess advantages of high durability and easy preparation [7]. Nevertheless, due to the low charge carrier mobility and conductivity of organic semiconductors, the efficiency of DSSCs employing solid-state hole-transporters is relatively lower than that of liquid-state DSSCs. In order to improve

the conductivity of organic semiconductors, molecular doping method has been investigated [8,9]. In 1998, Grätzel and co-workers [10] reported the first efficient all solid-state DSSC ($\eta = 0.74\%$) utilizing an organic semiconductor, 2,2′7,7′-tetrakis(*N,N*-di-p-methoxyphenylamine)-9,9′-spiro-bifluorene (spiro-MeOTAD), and a dopant, $N(PhBr)_3SbCl_6$. Through optimization, Grätzel and co-workers successfully improved the efficiency of kind of DSSCs to 2.56% [11] and 3.2% [12].

Poly(2-methoxy,5-(2′-ethyl-hexoxy)-1,4-phenylenevinylene) (MEHPPV), which has been widely used in organic solar cells [13,14], shows good functions in light absorption and hole transporting. To our knowledge, however, no report has been seen about the application of MEHPPV as a hole-transporting layer along with dye as sensitizer in DSSCs. Here, we employed MEHPPV in our solid-state DSSCs and improved the photovoltaic performance of such DSSCs by iodine doping in the MEHPPV layer. Iodine doping has been investigated in organic solar cells [8] and DSSCs [15,16]. Senadeera et al. [15] reported in 2002 that by iodine doping the pentacene based solid-state DSSCs showed an efficiency of 0.8%. What we reported here is not only the performance difference between doped and

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undoped DSSCs but also the fundamental principle of iodine doping in MEHPPV layer. It is found that due to the iodine introduction the photocurrent was improved by a factor of 5.5 and the incident photo-to-current conversion efficiency (IPCE) was also improved by almost 4 times at the peak absorption wavelength. In order to explore the surface state, charge distribution and conduction type of MEHPPV with and without iodine, surface photovoltage spectroscopy (SPS) along with electric-field-induced surface photovoltage spectroscopy (EFISPS) has been employed. Our experimental results show that MEHPPV film made from chloroform solution is characteristic of n-type conduction and the iodine doping leads to a change of the conduction type from n-type to p-type. It was suggested that such conduction type change is responsible for the improvement of the cell performance.

2. Experimental

2.1. Preparation of samples

TiO$_2$ colloid dispersion was prepared by following the procedure as reported in literature [17]. A compact TiO$_2$ layer (8 nm in thickness) was firstly deposited on the ITO glass (15 Ω/cm) in order to improve the ohmic contact and adhesion between porous TiO$_2$ layer and the conductive ITO glass. A porous TiO$_2$ film was formed by spin-coating from the colloid solution. The films were then thermo-treated at 450 °C for 30 min and taken out of the oven at ~100 °C and placed in 5 × 10^{-4} mol/l ethanolic solution of dye "N3", *cis*-(SCN)$_2$bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium. The thickness of the porous TiO$_2$ film was about 700 nm. The dye was synthesized according to the previous report [3]. After the TiO$_2$ coated substrate dying overnight, an 80 nm-thick MEHPPV (ADS 200RE, M_w = 300,000) film was spin-coated on top of the sensitized nanoporous TiO$_2$ layer from chloroform solution. Au layer (10 nm) as the back contact electrode and a 90 nm-thick Ag layer were formed by vacuum evaporation sequentially on the surface of MEHPPV layer. Iodine doping was performed by spin-coating a saturated iodine-hexane solution on the dye-sensitized TiO$_2$ film before MEHPPV film was formed. The doping level was controlled by the speed and time of spin-coating, which was 2000 rpm and 20 s, respectively. However, accurate control or estimation of the quantity of iodine inside MEHPPV film is difficult because vacuum deposition process, light illumination, and exposure to air would release iodine.

2.2. Measurements

The *I–V* curves were taken by KEITHLEY 4200 under irradiation of white light (20 mW/cm^2) from a Xe lamp with an active area of 0.25 cm^2. SPS and EFISPS were carried out with a solid junction photovoltaic cell: glass/Ag/(iodine)MEHPPV/Ag. The set-up of the measurement of SPS and EFISPS is as described in previous work
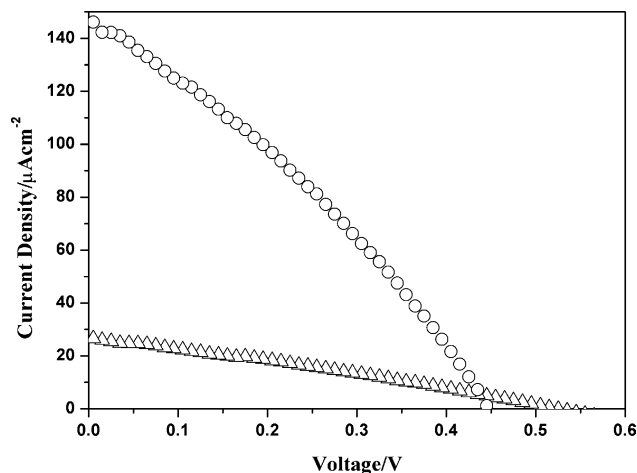

Fig. 1. Current–voltage characteristics at an illumination of 20 mW/cm^2 for a standard device without iodine doping (triangle) and a device with iodine doping (circle). The active electrode area is 0.25 cm^2.

[18]. Monochromatic light was obtained by passing light from a 200 W tungsten bromine lamp through a double-prism monochromator (CVI DK242). A lock-in amplifier (Stanford Research SR830) synchronized with a light chopper was employed to amplify the photovoltage signal. The spectra were normalized according to the intensity distribution of the light source. The IPCE was also determined by the above system where the photocurrent signal was recorded.

3. Results and discussion

Fig. 1 presents the current–voltage characteristics of the cells with undoped or doped MEHPPV layer, the corresponding cell performance is shown in Table 1. The current–voltage characteristics of the cell in the dark are also shown in Fig. 2. The cell with an undoped MEHPPV layer showed an inferior performance with an especially low short-circuit current density (I_{sc}) of 27 μA/cm^2 and a conversion efficiency of 0.02%. However, iodine doping resulted in a great improvement of I_{sc}, which was increased to 148 μA/cm^2, more than 5 times that of the undoped cell. With a slightly decreased open-circuit voltage and an increased fill factor, the overall conversion efficiency was increased to 0.1% due to iodine doping.

The IPCE results are shown in Fig. 3 from which we can see that the IPCE of the iodine doped DSSC was 3.9% at

Table 1
Summary of the photovoltaic performance at an illumination intensity of 20 mW/cm^2 for a reference device without iodine doping (1), and a device with iodine doping (2)

Device	V_{OC} (mV)	I_{sc} (μA/cm^2)	FF (%)	η (%)
1	521	27	28.6	0.02
2	448	148	31.2	0.1

J_{sc}, short-circuit current density; V_{OC}, open-circuit voltage; FF, fill factor; η, conversion efficiency. MEHPPV serves as hole conductor.

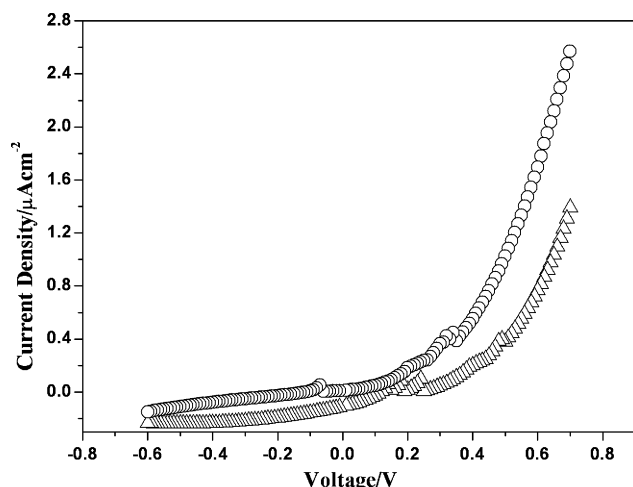Fig. 2. Current–voltage characteristics of undoped (triangle) and doped (circle) cells in the dark. The active electrode area is 0.25 cm^2.

Fig. 4. SPV spectra of MEHPPV film (square) and iodine doped MEHPPV film (triangle). Curves were normalized according to the wavelength distribution of light source.

the peak absorption wavelength while that of the undoped DSSC was only 1.0% at the same wavelength. This result is consistent with the above result that the overall photocurrent was increased by several times when iodine was doped into MEHPPV. It is found that the profile of photo-to-current action spectrum of iodine doped MEHPPV remains the same as that of undoped MEHPPV, indicating that the iodine doping did not change the photon absorption.

It has been reported that molecular doping would improve the performance of photovoltaic cells [8,9,15,16,19], most of which ascribed the enhancement of photocurrent to the increase of the carrier density and carrier mobility [8,9]. We can see from Table 1 that the fill factor was increased due to iodine doping, however, such an increase cannot be ascribed to the suppression of carrier recombination as the dark current shown in Fig. 2 also increased when iodine was introduced. The possible cause of the photocurrent improvement is the increase in conductivity of the hole-transporter.
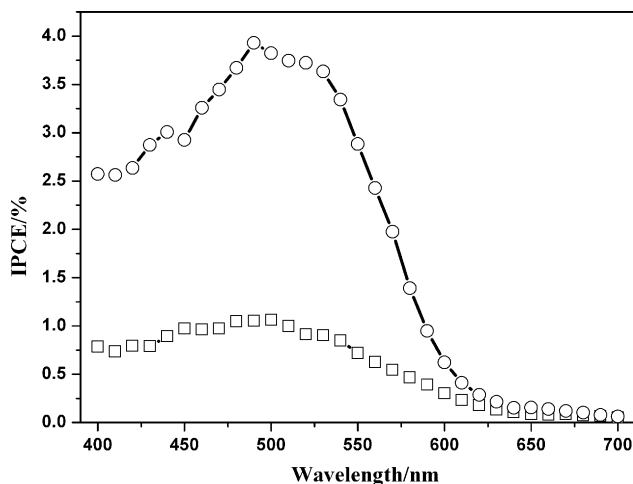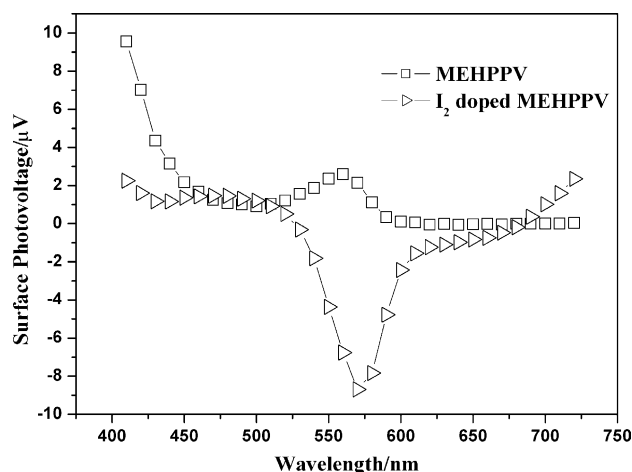

Fig. 3. IPCE of solid-state dye sensitized solar cells in the absence (square) and presence (circle) of iodine in the hole conductor matrix.

In order to investigate the underlying reason for the performance improvement, we employed SPS and EFISPS to study the hole conducting property of MEHPPV layer (undoped and doped). In principle, a surface photovoltage (SPV) arises from the excessive free carriers generated by photoexcitation and the following carrier redistribution [20]. Such carrier redistribution will change the potential distribution, especially the surface potential. EFISPS is a technique that combines the electric field with SPS. When a d.c. electric field is applied to the two sides of the film, the motion direction and diffusion distance of photogenerated charge carriers can be varied, resulting in the change of the built-in field of the film surface [21]. Fig. 4 shows the SPV spectra of undoped MEHPPV and doped MEHPPV. According to the previous study [22], the peak response between 450 nm and 600 nm corresponds to the π–π^* transition of MEHPPV molecules. It can be seen from Fig. 4 that the SPV signal was reversed when iodine was doped into the MEHPPV layer, which means that iodine did change the charge distribution of MEHPPV. The profiles of action spectra were almost the same for the cells with and without iodine doping, that is to say, the iodine doping did not damage the MEHPPV film but cause a drastic shift of the Fermi level.

In our study, it is interestingly noted that the conduction type of MEHPPV varies with solvent. The solvent used here is chloroform, which is a non-aromatic solvent. The EFISPV spectra of MEHPPV is shown in Fig. 5 (the applied d.c. voltage is 0.8 V), from which we can learn that MEHPPV is a n-type semiconductor. The determination of the conduction type has been reported in literature as follows [23]: A change in surface potential ($\delta V_s = V'_s - V^0_s$) takes place when the semiconductor is illuminated, where V^0_s and V'_s are the surface potential heights before and after illumination, respectively. For an n-type semiconductor, the SPV response is negative ($\delta V_s < 0$) when no electric field is put on. If a positive electric field (the illuminated surface is positive) is applied vertically on the n-type semiconductor surface, elec-
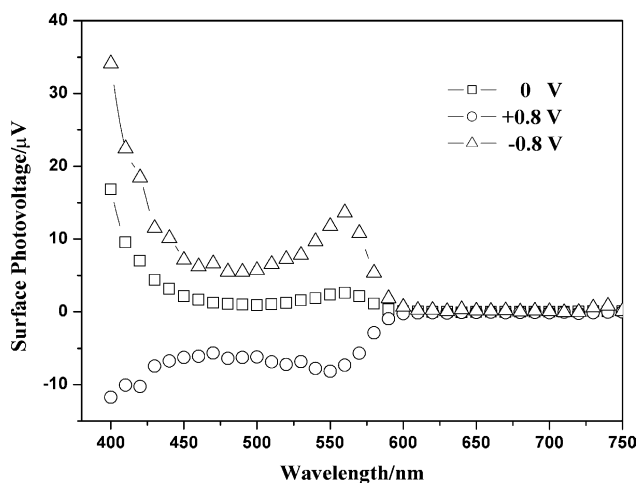
Fig. 5. EFISPV spectra of MEHPPV film under the bias of 0 V (square), +0.8 V (circle) and −0.8 V (triangle).

trons move to the surface while holes move to the bulk so that the built-in field is enhanced and the surface band bending increases upward, and even the SPV response turns to positive ($\delta V_s < 0$). If a negative electric field is applied, whose direction coincides with that of the built-in field, the surface band bending decreases to a lower level. Generally, δV_s is less than zero but the intensity of SPV response increases in original direction. In contrast to the n-type semiconductor, the SPV response intensity of a p-type semiconductor increases in the same direction as a positive field is applied and reduces as a negative electric field is applied.

When the iodine was doped into MEHPPV, the EFISPS was different from the original one, which is shown in Fig. 6. From the above discussion, we can see that iodine doping converted the n-type MEHPPV to p-type MEHPPV. Tengfeng Xie et al. [23] have studied the undoped and iodine doped azo-pigment film and demonstrated a conversion of conduction type from n-type to p-type. Since the iodine in the semiconductor bulk can act as an acceptor of electrons from the va-
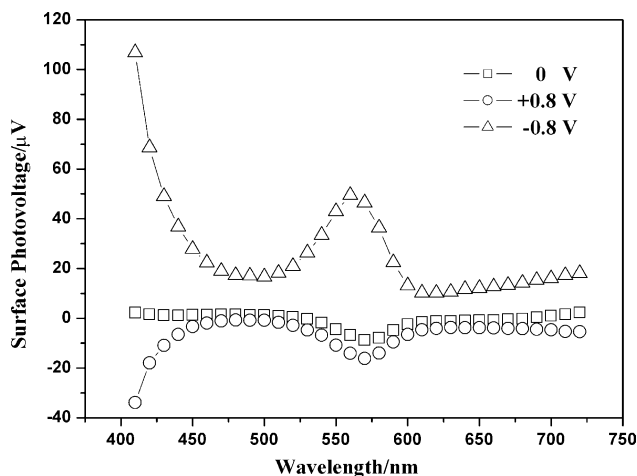
lence band to induce p-type conductivity [16], we can explain the change of the conduction type according to the Poisson equation:

$$\frac{d^2\phi}{dx^2} = -\frac{\rho}{\kappa\varepsilon_0} \qquad (1)$$

where ρ is the charge density (C/m^3), κ is the dielectric constant, ε_0 is the permittivity of free space, and the relationship between V_s and N_A, N_D can be deduced as the below equation:

$$V_s = e(N_D - N_A)W^2/2\kappa\varepsilon_0 \qquad (2)$$

where V_s is the built-in potential at the Schottky barrier junction, e the electronic charge, W the depletion width, N_A the concentration of ionized acceptors, N_D the concentration of donors.

In our system, N_D stands for the concentration of MEH-PPV, which is an approximate constant, and N_A represents the concentration of iodine. Iodine molecules introduced into the MEHPPV film can draw the electrons from the ground state of MEHPPV. A positive shift of the Fermi level of MEHPPV takes place and the Fermi level reaches the nearby valence band. Therefore according to Eq. (2), V_s decreases, even in the reverse direction with enough quantity of iodine, that is, the direction of the surface band bending of the iodine doped MEHPPV is reversed. As a result, the carriers photogenerated near the photoactive Ag/MEHPPV interface move in the opposite direction. The SPV response of iodine doped MEHPPV film is opposite to that of MEHPPV film. Since the p-type conductivity is of great importance for solid state DSSCs, we ascribed the increase of photocurrent to such a change of conduction type from n to p.

From Fig. 1 we can see that the open-circuit voltage of iodine doped DSSC was lower than that of undoped DSSC. It can be explained by Fig. 2, which shows an increase in dark current when iodine was introduced. This result means that the recombination was enhanced and the rectifying characteristics became poorer. V_{OC} can be determined by the below formula:

$$V_{OC} = \frac{kT}{e} \ln \frac{I_{inj}}{n_{cb}k_{et}[p^+]} \qquad (3)$$

where k and T are the Boltzmann constant and absolute temperature, I_{inj} the flux of charge resulted from electron injection from the sensitizing dye, n_{cb} the concentration of electrons at the TiO$_2$ surface, and k_{et} the rate constant of recombination. It is obvious that V_{OC} decreases with increased k_{et}. What should be noted is that the probability of short-circuiting to back contact via open voids will possibly increase as the conductivity of hole transporting layer increases. This will also reduce the open-circuit voltage along with the rectifying properties of DSSCs.

Fig. 6. EFISPV spectra of iodine doped MEHPPV film under the bias of 0 V (square), +0.8 V (circle) and −0.8 V (triangle).

4. Conclusion

In conclusion, the influence of iodine doping on the photovoltaic performance of DSSC employing MEHPPV as the hole-transporter was investigated. When iodine was introduced into the MEHPPV layer the photocurrent was increased from $27\,\mu A/cm^2$ to $148\,\mu A/cm^2$, and the IPCE and overall efficiency also had a remarkable improvement. It has been demonstrated through SPS and EFISPS study that MEHPPV film made from chloroform solution owns n-type conduction, and the iodine doping changed its conduction type to p-type, leading to the conclusion that iodine doping improved the p-type conductance of MEHPPV by an extraordinary magnitude. An increase in conductivity of MEHPPV by iodine doping was also confirmed by the increase of fill factor, which is partially responsible for the improvement of the cell performance.

References

[1] B. Oregan, M. Grätzel, Nature 335 (1991) 737–740.

[2] M. Grätzel, Nature 335 (2001) 338–344.

[3] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrybaker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 335 (1993) 6382–6390.

[4] E. Stathatos, P. Lianos, A.S. Vuk, B. Orel, Adv. Funct. Mater. 335 (2004) 45–48.

[5] P. Wang, S.M. Zakeeruddin, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Grätzel, Nat. Mater. 335 (2003) 402–407.

[6] B. O'Regan, D.T. Schwartz, S.M. Zakeeruddin, M. Grätzel, Adv. Mater. 335 (2000) 1263.

[7] D. Gebeyehu, C.J. Brabec, N.S. Sariciftci, Thin Solid Films 335 (2002) 271–274.

[8] J.H. Schon, C. Kloc, E. Bucher, B. Batiogg, Nature 335 (2000) 408–410.

[9] M. Rudiono, Takeuchi, Jpn. J. Appl. Phys. Part 2, Lett. 335 (1997) L127-L129.

[10] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Grätzel, Nature 335 (1998) 583–585.

[11] J. Kruger, R. Plass, L. Cevey, M. Piccirelli, M. Grätzel, U. Bach, Appl. Phys. Lett. 335 (2001) 2085–2087.

[12] J. Kruger, R. Plass, M. Grätzel, H.J. Matthieu, Appl. Phys. Lett. 335 (2002) 367–369.

[13] J. Liu, Y.J. Shi, Y. Yang, Adv. Funct. Mater. 335 (2001) 420–424.

[14] M.Y. Song, J.K. Kim, K.J. Kim, D.Y. Kim, Synth. Met. 335 (2003) 1387–1388.

[15] G.K.R. Senadeera, P.V.V. Jayaweera, V.P.S. Perera, K. Tennakone, Sol. Energy Mater. Sol. Cells 335 (2002) 103–108.

[16] V.P.S. Perera, K. Tennakone, Sol. Energy Mater. Sol. Cells 335 (2003) 249–255.

[17] C.J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, J. Am. Ceram. Soc. 335 (1997) 3157–3171.

[18] D.J. Wang, J. Zhang, T.S. Shi, B.H. Wang, X.H. Cao, T.J. Li, J. Photochem. Photobiol. A: Chem. 335 (1996) 21–25.

[19] J.H. Schon, C. Kloc, E. Bucher, B. Batlogg, Synth. Met. 335 (2000) 177–180.

[20] D. Gal, Y. Mastai, G. Hodes, L. Kronik, J. Appl. Phys. 335 (1999) 5573–5577.

[21] X.M. Qian, D.Q. Qin, Q. Song, Y.B. Bai, T.J. Li, X.Y. Tang, E.K. Wang, S.J. Dong, Thin Solid Films 335 (2001) 152–161.

[22] B.N. Kang, G.T. Du, Z.H. Huang, Y. Qiu, Synth. Met. 335 (2003) 1513–1514.

[23] T.F. Xie, D.J. Wang, L.J. Zhu, C. Wang, T.J. Li, X.Q. Zhou, M. Wang, J. Phys. Chem. B 335 (2000) 8177–8181.