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Highly efficient cosensitization of D-A-π-A benzotriazole organic dye with porphyrin for panchromatic dye-sensitized solar cells

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Comparing with the development of novel organic sensitizers, cosensitization is a much more convienient way to acquire panchromatic dye-sensitized solar cells (DSSCs). Taking the strong absorption in long wavelength region but lack response in ranges of 350 - 410 nm and 500 - 600 nm of porphyrin dyes into account, the D-A- π -A benzotriazole organic dye (**WS-5**), showing strong absorption bands in these two ranges, is targeted for cosensitization with porphyrin dye **XW4**. The cosensitization effects in light-harvesting capability, photovoltaic performance, charge recombination as well as long-term stability have been investigated in detail, especially for the interactions between **WS-5** and **XW4** and their effects in photovoltaic performance. Noticeably, the strong panchromatic light response and the promising photovoltaic efficiency of 10.41% has been achieved with only 6 μ m TiO₂ film, which is obviously higher than the corresponding efficiencies obtained using single sensitizer. The cosensitization is essentially dominated by **WS-5** while only small amount of **XW4** is contributed to enhance the IPCE response in long wavelength region. These results demonstrate the effective approach for utilizing porphyrin dyes to simultaneously fill up the absorption valleys of D-A- π -A featured sensitizers and promote the DSSC efficiency , presenting the effective strategy of cosensitization to combine the advantages of both porphyrin and organic dyes, especially for pursuring highly efficient panchromatic dye-sensitized solar cells.

Introduction

As one of the key components of DSSCs, the organic sensitizers based on donor- π -acceptor (D- π -A) motif have been extensively explored in the last decade due to their high molar extinction coefficients, rare-metal-free structures, and most importantly the facile molecular tailoring with tunable photovoltaic performances.¹⁻³ However, compared to metal complex sensitizers, organic dyes generally bestow one narrow absorption band in visible region, leading to a serious energy waste.⁴⁻⁶ Recently, porphyrin dyes, possessing two major absorption bands in visible region: strong Soret band around 450 nm and relatively weak Q band around 650 nm, have attracted considerable interests with great breakthrough in power-conversion efficiency (PCE).⁷⁻⁹ Up to date, porphyrin dyes based on D- π -A system are still the most successful kind of organic sensitizers, such as **GY50** (12.75%)¹⁰ and the record

^aShanghai Key Laboratory of Functional Materials Chemistry, Key Laboratory for Advanced Materials and Institute of Fine Chemicals, Collaborative Innovation Center for Coal Based Energy (i-CCE), East China University of Science and Technology, Shanghai 200237, P. R. China. E-mail: <u>whzhu@ecust.edu.cn</u>. one **SM315** (13.0%) based on cobalt electrolytes.¹¹ However, even as efficient as **GY50** and **SM315**, typical porphyrin dyes still have their intrinsic drawback: the extremely weak absorption in region of 350 - 410 nm and 500 - 600 nm, which is difficult to overcome by molecular engineering of porphyrin structure.⁷ Thus, taking the respective advantage and disadvantage of organic sensitizers and porphyrin sensitizers into account, the cosensitization method,¹²⁻¹⁷ which has been exploited with one or more kinds of small dyes co-adsorbed onto the porphyrin-sensitized TiO₂ photoanode, has attracted more and more attentions. Besides the favorable π -aggregation prevention effect on TiO₂ surface,^{12b} more importantly, the small dyes may also can well complement the absorption spectra of porphyrin dyes.

As mentioned above, to be the proper candidate for the cosensitization with porphyrin dyes, the small dyes should possess strong absorption in the ranges of 350 - 410 nm and 500 - 600 nm. Recently, a series of D-A- π -A indoline dyes with auxiliary acceptor were developed and applied as the highly efficient sensitizer in DSSCs (**WS** series).¹⁸⁻²² By screening different auxiliary acceptor with different electron withdrawing capabilities, the absorption band of these dyes can be shifted in broad range. Among all these dyes, **WS-5**,¹⁹ with benzotriazole as the auxiliary acceptor, shows high light-



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harvesting capability in region of 350 - 420 nm and 450 - 650 nm, which exactly complements the deficiencies of porphyrin dyes, suggesting that **WS-5** may be a promising cosensitizer of porphyrin dyes. However, the spatial distribution and the intermolecular interactions between the co-adsorbed dyes, such as the adsorption competition, suitable size, shape, orientation and depth profile composition are also key factors as well as compensating light-harvest in the cosensitization strategy.¹⁴ Among them, the adsorption competition is the most important factor, which affects the dye-loaded ratio directly. As a consequence, it is far away from exploring a suitable couple of dyes to successfully cosensitize TiO₂ electrode with high efficiency.

With these concerns in mind, herein, **WS-5** was cosensitized with an efficient porphyrin dye **XW4** (Scheme 1),²³ and the cosensitization effects on light-harvesting capability, photovoltaic performance, charge recombination, and long-term stability have been investigated in detail, especially for the interactions between **WS-5** and **XW4**. Accordingly, the cosensitized cells achieved strong panchromatic light harvesting and the highest efficiency of 10.41% with only 6 μ m TiO₂ film, obviously higher than the corresponding efficiencies obtained using single sensitizer. These results demonstrate the effective approach for utilizing D-A- π -A featured sensitizers to simultaneously fill up both of the absorption valleys of porphyrin dyes and promote the DSSC efficiency. Moreover, highly efficient panchromatic cosensitized DSSCs may be developed.



Scheme 1 Molecular structures of dyes WS-5 and XW4.

Experimental

Materials

The FTO conducting glass (OPV-FTO22-7, fluorine doped SnO₂, sheet resistance 7 - 8Ω /square, transmission 75 - 80%) was obtained from OPV Tech Co., Ltd. *Tert*-butylpyridine (TBP), titanium tetrachloride, lithium iodide, 1-methyl-3-propyl-imidazolium iodide (PMII), and 1-butyl-3-methylimidazolium iodide were purchased from Adamas and used as received. Transparent TiO₂ paste (18NR-T) was purchased from Dyesol Ltd. Light-scattering anatase particle was obtained from the Shanghai Institute of Ceramics. All other chemicals used were produced by *J&K* and used without further purification.

DSSCs fabrication

All working electrodes used in this work were prepared and modified following the reported procedure.²⁴ The films were then immersed into a 0.3 mM solution of WS-5 in a mixture of chloroform and ethanol (volume ratio of 1 : 1) at 25 °C for 12 h or a 0.2 mM solution of XW4 in a mixture of toluene and ethanol (volume ratio of 1 : 4) at 25 °C for 12 h. For cosensitization, WS-5/XW4-sensitized films were washed with ethanol, dried in air, and then immersed in a solution containing the WS-5/XW4 and kept at 25 °C for different time. The counter electrode was prepared by sputtering with three drops of 0.02 M H₂PtCl₆ in 2-propanol followed by annealing treatment at 400 °C for 15 min. A hole (diameter of 0.8-mm) was drilled on the counter electrode. For the assembly of DSSCs, the two electrodes were sandwiched using a 25 μm thick hot-melt gasket. The cell area was controlled to be 0.12 cm⁻² for photovoltaic performance measurements and 3.22 cm⁻² for photophysical and dye-loaded amount measurements. In this work, 0.1 M Lil, 0.05 M I₂, 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile were used as the redox electrolyte. The quasisolid-state electrolyte was obtained from HeptaChroma (DMPII/DMII/BMII/PMII). All data shown in this work were the average values of five parallel tests.

Photovoltaic performance measurements

The UV-vis absorption spectra were measured by CARY 100 spectroscopy. The photocurrent-voltage (I-V) curves were obtained under AM1.5G simulated solar light by illuminating the cell through the FTO substrate from the photoanode side. The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. The incident photon-to-charge carrier efficiencies (IPCEs) were obtained on a Newport-74125 system (Newport instruments). The intensity of monochromatic light was detected by a Si detector (Newport-71640). The electrochemical impedance spectroscopy (EIS) measurements of all DSSCs were performed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany), with the frequency range of 0.1 Hz-100 kHz and the alternative signal of 5 mV. The bias potential varied between 600 and 800 mV with about 50 mV progressive increase, and the spectra was characterized with Z-View software. The aging time test was measured in air under visible-light soaking at 25 °C.

Results and discussion

As shown in Fig. 1a, XW4 bestows an intense Soret band in the range of 400 - 480 nm and less intense Q bands in the range of 630 - 700 nm, with very weak absorption between 350 and 400 nm, as well as between 480 and 630 nm, which are typical features of porphyrins in absorption spectrum. In contrast, cosensitizer **WS-5** demonstrates a broad absorption bands at around 390 and 500 nm, ¹⁹ which compensates well the poor absorption of XW4. Moreover, the absorption spectra of **WS-5** and XW4 on TiO₂ film were shown in Fig. 1b. Although the

absorption peaks of **WS-5** and **XW4** are bathochromically shifted relative to those in solution, the absorption bands of both dyes are broadened obviously. Furthermore, according to their absorption spectra on TiO_2 film, **WS-5** and **XW4** maybe a promising couple for the cosensitization application. Thus, in view of spectrum compensation, the absorbance as a function of dipping time were measured firstly for **XW4**, **WS-5**, and cosensitized one, respectively, to optimize the cosensitization procedure (Fig. 2).



Fig. 1 Absorption spectra of dyes WS-5 and XW4: (a) in THF and (b) anchored on a 3 μm TiO_2 film.

After 12 h adsorption in XW4, the absorbance of the dyeloaded TiO₂ electrode remained at the same level, meaning that XW4 needs over 12 h to reach its saturated adsorption (Fig. 2a). In case of WS-5, the saturated adsorption duration was only around 4 h. To be noticed, after dipping for only 2 h, 97% of saturated adsorption has been achieved by WS-5, showing much faster adsorption rate with respect to XW4. Obviously, WS-5 is much more easily to adsorb on TiO₂ surface, that is, if the TiO₂ electrode was sensitized by WS-5 first or sensitized in WS-5/XW4 mixed solution, XW4 was difficult to compete with WS-5 and adsorb enough amount on TiO₂ electrode. Thus, in the following optimization and evaluation, the TiO₂ electrodes were prepared by dipping in XW4 solution for 12 h and then dipping in WS-5 solution for different period.



Fig. 2 Absorbance as a function of dipping time for XW4-sensitized, WS-5sensitized, and mixture cosensitized one on 6 μ m transparent TiO₂ film.

To further investigate the adsorption behavior of XW4 and WS-5, the corresponding absorption spectra of XW4-sensitized TiO₂ dipping in WS-5 solution for different time were measured (Fig. 2c). The absorbance of Q band of XW4 quickly decreased to around half of original value after dipping in WS-5 solution for only 0.5 h, indicating that except for the adsorption on unoccupied TiO₂ surface, a fierce competition took place between WS-5 and XW4, and XW4 was quickly replaced by WS-5. Accordingly, along with the increase of absorption in region of 500 - 600 nm, the light harvesting capability in long wavelength region originated from XW4 seriously decrease. Thus, the increase in short wavelength and the decrease in long wavelength should be well balanced to obtain the best performance. The IPCE action spectra of all these cosensitization electrodes were measured and shown in Fig. 3.



Fig. 3 IPCE as a function of wavelength for different XW4/WS-5 cosensitized DSSCs. The TiO₂ electrodes were consist of 6 μ m transparent layer and 8 μ m scattering layer.

Table 1 Photovoltaic parameters of WS-5/XW4 cosensitized DSSCs by cosensitization with WS-5 for different time.^a

Device	Dipping time	J _{sc} mA cm ⁻²	V _{oc} mV	FF	η %
А	0 h	13.01±0.86	714±6	0.70±0.02	6.42±0.19
В	0.5 h	19.36±0.10	733±3	0.73±0.80	10.27±0.09
С	1.0 h	19.52±0.82	741±1	0.71±0.02	10.28±0.18
D	2.0 h	19.58±0.43	747±2	0.69±0.01	10.18±0.09
Е	2.5 h	18.79±0.48	774±7	0.72±0.01	10.41±0.14
F	4.0 h	16.03±0.27	803±10	0.70±1.20	9.02±0.55

^aThe TiO₂ electrodes were consist of 6 μ m transparent layer and 8 μ m scattering layer, while a mixture of 0.1 M LiI, 0.05 M I₂, 0.6 M 1-methyl-3-propyl-imidazolium iodide (PMII), and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile was used as the redox electrolyte.

Upon cosensitization with WS-5 for 0.5 h, the IPCE values in the range of 350 - 650 nm have been effectively improved due to the strong light conversion capability of WS-5 in this range. Besides, quite interesting tendency of IPCE value at 680 nm has also been observed. With the cosensitization of WS-5 for 0 - 1.0 h, the IPCE680 nm was increased from 54% to the maximum value of 68%. However, when the dipping time was continually extended to 4 h, a negative contribution to the IPCE has been observed, that is the $\mathsf{IPCE}_{\mathsf{680}\,\mathsf{nm}}$ was gradually decreased to be only 40%. It is indicative that WS-5 replaces XW4 on the surface of TiO₂ due to its higher adsorption capacity, which is consistent with the results of absorption spectra.^{12,15} As a result, after cosensitizing with WS-5 for only 0.5 h, the J_{sc} successfully realized a huge increase from 13.01 to 19.36 mA cm^{-2} (Table 1). Obviously, except for the complement of the light response area, WS-5 also acted as a co-absorbent material, such as DCA, to break the π -aggregation of **XW4** on the surface of the TiO₂ electrode. Along with the increase of the dipping time from 0.5 to 2.0 h, the $J_{\rm sc}$ was slightly enhanced from 19.36 to 19.58 mA cm⁻². When the cosensitization extended for over 2.0 h, the J_{sc} was decreased apparently, which was caused by the sharp decrease of IPCE values in long wavelength region. While the cosensitization was last for 2h, which presented the highest $J_{\rm sc}$ value, the

absorbance of Q band of **XW4** was only around 20% of the original value, corresponding to a ratio between **XW4** and **WS-5** of 1/16 (Table 2). Accordingly, the cosensitization was actually dominated by **WS-5** while only small amount of **XW4** was utilized to enhance the IPCE response in long wavelength region.

Table 2 Dye-loaded amounts of XW4-, WS-5-, and cosensitized on $~6~\mu m$ transparent TiO_2 film evaluated by desorption method.

Dye	Time / h	Dye-loaded amount/10 ⁻⁷ molcm ⁻²		
XW4	12.0	0.47		
WS-5	12.0	1.89		
	0.5	0.279/0.72		
	1.0	0.081/0.85		
XW4/WS-5	2.0	0.054/0.88		
	4.0	0.046/0.94		
	12.0	0.012/1.33		

Besides, the cosensitized photoanodes in the reverse dipping order were also studied, that is, the TiO_2 electrodes were first immersed in **WS-5** for 12.0 h and then immersed in **XW4** for 0 - 2.0 h (Table 3), showing poorer performance than their corresponding devices (device B, C, D). For example, compared with device C, the efficiency of device was decreased to 8.35%, with J_{sc} of 16.30 mA cm⁻², V_{oc} of 750 mV, and FF of 0.67, under the same conditions.

Table 3 Photovoltaic parameters of DSSCs with WS-5-sensitizaed TiO_2 electrode for 12h cosensitized by XW4 for different time.^a

Device	Dipping time	J _{sc} mA cm ⁻²	V _{oc} mV	FF	η %
G	0 h	16.20±0.22	790±8	0.67±0.01	8.64±0.20
Н	0.5 h	17.34±0.22	718±3	0.65±0.01	8.00±0.20
I	1.0 h	16.30±0.50	750±10	0.67±0.01	8.35±0.20
J	2.0 h	15.66±0.31	750±5	0.69±0.01	8.08±0.15

^a The TiO₂ electrodes were consist of 6 μ m transparent layer and 8 μ m scattering layer, while a mixture of 0.1 M LiI, 0.05 M I2, 0.6 M 1-methyl-3-propyl-imidazolium iodide (PMII), and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile was used as the redox electrolyte.

Actually, when carefully comparing the J_{sc} with different adsorption sequence, the cosensitization effect is quite different. While the electrode was sensitized by **XW4** then cosensitized by **WS-5** for 0.5 - 2.0 h (**WS-5/XW4**), the J_{sc} values stayed at the same level and showed slightly increase. In contrast, while the electrode was sensitized by **WS-5** then cosensitized by **XW4** for 0.5 - 2.0 h (**WS-5/XW4**), the J_{sc} values decreased obviously. A plausible explanation is that small molecular volume of **WS-5** can guarantee the dye adsorb on the unoccupied TiO₂ surface but not replace **XW4**. However, in case of **WS-5/XW4**, **XW4** with large molecular volume is difficult to adsorb on TiO₂, which was crowdedly covered by **WS-5**, without replacement of **WS-5**, thus resulting in the

efficient

decrease of overall dye-loaded amount. Accordingly, by using **WS-5/XW4** cosensitized TiO₂ electrode, very promising PCE of 10.41% was achieved, with J_{sc} of 18.79 mA cm⁻², V_{oc} of 774 mV, and FF of 0.72. Furthermore, the PCE remained at 98% of the initial value after 1000 h in aging test, demonstrating the high stability of cosensitized DSSC device (Fig. 4).



XW4/WS-5 cosensitized DSSC under visible-light soaking.

To be noticed, along with the increase of the dipping time from 0 to 4.0 h, the $V_{\rm oc}$ was also increased from 714 to 803 mV. As known, with use of fixed redox species, the $V_{\rm oc}$ is only determined by the Fermi level (E_{Fn}) of TiO₂, which is affected by the conduction band of TiO_2 (E_{CB}) and the charge recombination rate.^{1b} Therefore, cosensitization can not only patch up the lack of light harvesting to enhance the J_{sc} , but also can optimize the E_{CB} or the interfacial charge transfer process to enhance the $V_{\rm oc}$. To gain insight into the effect of cosensitization on V_{oc} the eletrochemical impedance spectroscopy (EIS) was performed on WS-5-, XW4-, and WS-5/XW4 sensitized DSSCs and shown in Fig. 5. The fitted capacitive (C_u) response of three devices was shown in Fig.5a. The logarithm of C_{μ} was increased linearly with the given bias potential, and all the curves exhibited the same slope. Moreover, at fixed potential, the C_{μ} values of all three devices are the same, indicating that the E_{CB} values of three devices are at the same level. That means the increase of $V_{\rm oc}$ should originate from the prevention of interfacial charge recombination. Thus, the recombination resistance (R_{CT}) values were further measured (Fig. 5b). At fixed potential, the $R_{\rm rec}$ of three devices lay in order of WS-5>WS-5/XW4>XW4, in good agreement with their similar $V_{\rm oc}$ values (Table 1 and Table 3). The increase of cosensitization device in $V_{\rm oc}$ should be predominantly arisen from the repression of charge recombination. Thus, the charge lifetimes (τ) of three devices were calculated according to $\tau = C_{\mu}R_{CT}$, and shown in Fig. 5c. At fixed potential, taking 0.70 V for example, the τ values of three devices were calculated to be 0.14, 0.01, and 0.05 S, respectively. Obviously, the introduction of the coadsorbent



with bulk chain such as WS-5 can distinctly repress the charge

recombination rate, thus resulting in the

enhancement in V_{oc} from 714 to 774 mV.

Fig. 5 Plot curves under a series potential bias of DSSCs based on reference dye **WS-5**, **XW4**, and cosensitization of **WS-5** and **XW4**: (a) cell capacitance (C_{μ}) , (b) recombination resistance (R_{CT}) , and (c) calculated electron lifetime (τ).

Finally, to facilitate feasible applications, the DSSCs based on quasi-solid-state electrolyte were also prepared. Compared to the devices based on liquid electrolyte, only slight decrease was found in J_{sc} and V_{oc} (Fig. 6). Thus, the major factor of sharp decrease in PCE was the obvious reduction in FF from 0.72 to 0.63, which caused by the increase of charge transfer resistance in quasi-solid cell device.



Fig. 6 *I-V* curves of **WS-5/XW4** cosensitized DSSC using quasi-solid-state electrolyte compared to the one based on liquid electrolyte.

Conclusions

Cosensitization based on multiple dyes as "dye cocktails" has been focused, especially in compensating and broadening the light response region. Exploring organic dye WS-5 and porphyrin XW4 as the cosensitized couple, the light harvesting defect of each single dye has been sufficiently overcome. Besides, with long alkyl chain on the additional acceptor in D-A- π -A featured organic dye, WS-5 could also prevent the charge recombination effectively, leading to a great enhancement in V_{oc} . As a result, a very promising overall photovoltaic efficiency of 10.41% with long-term stability was achieved (J_{sc} = 18.79 mA cm⁻², V_{oc} = 774 mV, and FF = 0.72). Furthermore, the PCE remains at 98% of the initial value after 1000 h in aging test, demonstrating the high stability of cosensitized DSSC device. While utilizing quasi-solid state electrolyte, only a slight decrease was found in J_{sc} and V_{oc} . Our work well demonstrates the effective strategy of cosensitization to combine the advantages of both porphyrin and organic dyes, especially for developing highly efficient panchromatic DSSCs.

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Highly efficient cosensitization of D-A- π -A benzotriazole organic dye with porphyrin for panchromatic dye-sensitized solar cells

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Regarding the efficient cosensitization effects, the optimization between pure organic dye and porphyrin sensitizer and their effects in photovoltaic performance are focused, achieving the strong panchromatic light response and the promising photovoltaic efficiency of 10.41% with only 6 μ m TiO₂ film.

