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

Jingchuan Liu, a Bo Liu, a,b Yunyu Tang, a Weiwei Zhang, a Wenjun Wu, a Yongshu Xie a and Wei-Hong Zhu a*

Comparing with the development of novel organic sensitizers, cosensitization is a much more convenient 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 μm 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 pursuing 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 photoelectronic 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 GYSO (12.75%)10 and the record one SM315 (13.0%) based on cobalt electrolytes.14 However, even as efficient as GYSO 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,12,13 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-
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. 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), 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 μm 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.

**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, 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 TiO₂ 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 TiO₂ film.](image1)

![Fig. 2 Absorbance as a function of dipping time for XW4-sensitized, WS-5-sensitized, and mixture cosensitized one on 6 μm transparent TiO₂ film.](image2)

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.

After 12 h adsorption in XW4, the absorbance of the dye-loaded 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. 3 IPCE as a function of wavelength for different WS-5/WS-5 cosensitized DSSCs. The TiO$_2$ electrodes were consist of 6 μm transparent layer and 8 μm scattering layer.

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

<table>
<thead>
<tr>
<th>Device</th>
<th>Dipping time / h</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>$V_{oc}$ / mV</th>
<th>FF</th>
<th>η / %</th>
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<tr>
<td>A</td>
<td>0</td>
<td>13.01±0.86</td>
<td>714±6</td>
<td>0.70±0.02</td>
<td>6.42±0.19</td>
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<tr>
<td>B</td>
<td>0.5</td>
<td>19.36±0.10</td>
<td>733±3</td>
<td>0.73±0.10</td>
<td>10.27±0.09</td>
</tr>
<tr>
<td>C</td>
<td>1.0</td>
<td>19.52±0.82</td>
<td>741±1</td>
<td>0.71±0.02</td>
<td>10.28±0.18</td>
</tr>
<tr>
<td>D</td>
<td>2.0</td>
<td>19.58±0.43</td>
<td>747±2</td>
<td>0.69±0.01</td>
<td>10.18±0.09</td>
</tr>
<tr>
<td>E</td>
<td>2.5</td>
<td>18.79±0.48</td>
<td>774±7</td>
<td>0.72±0.01</td>
<td>10.41±0.14</td>
</tr>
<tr>
<td>F</td>
<td>4.0</td>
<td>16.03±0.27</td>
<td>803±10</td>
<td>0.70±0.12</td>
<td>9.02±0.55</td>
</tr>
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</table>

The TiO$_2$ electrodes were consist of 6 μm transparent layer and 8 μm scattering layer, while a mixture of 0.1 M LiI, 0.05 M I$_2$, 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 IPCE$_{580\text{ nm}}$ 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 IPCE$_{580\text{ nm}}$ was gradually decreased to be only 40%. It is indicative that WS-5 replaces XW4 on the surface of TiO$_2$ due to its higher adsorption capacity, which is consistent with the results of absorption spectra. 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 TiO$_2$ electrode. Along with the increase of the dipping time from 0.5 to 2.0 h, the $J_{sc}$ 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 $J_{sc}$ 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.

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.

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 TiO$_2$ surface but not replace XW4. However, in case of WS-5/XW4, XW4 with large molecular volume is difficult to adsorb on TiO$_2$, which was crowdedly covered by WS-5, without replacement of WS-5, thus resulting in the
decrease of overall dye-loaded amount. Accordingly, by using WS-5/XW4 cosensitized TiO₂ electrode, very promising PCE of 10.41% was achieved, with Jₘ, of 18.79 mA cm⁻², Vₘ, 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).

To be noticed, along with the increase of the dipping time from 0 to 4.0 h, the Vₘ, was also increased from 714 to 803 mV. As known, with use of fixed redox species, the Vₘ, is only determined by the Fermi level (Eₘ,) of TiO₂, which is affected by the conduction band of TiO₂ (EₖB) and the charge recombination rate. Therefore, cosensitization can not only patch up the lack of light harvesting to enhance the Jₘ, but also can optimize the EₖB or the interfacial charge transfer process to enhance the Vₘ,. To gain insight into the effect of cosensitization on Vₘ, the electrochemical impedance spectroscopy (EIS) was performed on WS-5-, XW4-, and WS-5/XW4 sensitized DSSCs and shown in Fig. 5. The fitted capacitive (Cₘ) response of three devices was shown in Fig.5a. The logarithm of Cₘ was increased linearly with the given bias potential, and all the curves exhibited the same slope. Moreover, at fixed potential, the Cₘ values of all three devices are the same, indicating that the EₖB values of three devices are at the same level. That means the increase of Vₘ, should originate from the prevention of interfacial charge recombination. Thus, the recombination resistance (Rₘ,) values were further measured (Fig. 5b). At fixed potential, the Rₘ, of three devices lay in order of WS-5>WS-5/XW4>XW4, in good agreement with their similar Vₘ, values (Table 1 and Table 3). The increase of cosensitization device in Vₘ, should be predominantly arisen from the repression of charge recombination. Thus, the charge lifetimes (τ) of three devices were calculated according to τ = CₘRₘ,, 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 efficient enhancement in Vₘ, from 714 to 774 mV.

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 Jₘ, and Vₘ, (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.
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 compared to the one based on liquid electrolyte.

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Notes and references


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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 μm TiO₂ film.