A Co-Sensitization Process for Dye-Sensitized Solar Cell: Enhanced Light-Harvesting Efficiency and Reduced Charge Recombination

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Abstract. A ruthenium complex dye (N719) and a metal-free phenothiazine-based dye (PTZ-4) were used for the co-sensitized dye-sensitized solar cell (DSSC), intending to achieve complementary absorption spectra and reduce charge recombination, thereby improvement in the performance. Upon co-sensitization, the device made of the N719+PTZ-4 system yielded short-circuit photocurrent density ($J_{sc}$) of 16.69mA cm$^{-2}$, open circuit voltage ($V_{oc}$) of 0.75V, fill factor (FF) of 0.67 and power conversion efficiency (PCE) of 8.42%; this performance is superior to that of either individual device made from dye N719 (PCE=7.11%) or dye PTZ-4 (PCE=5.14%). The improved performance ascribes to effectively enhance light-harvesting efficiency and reduce charge recombination by the co-sensitization process.

1. Introduction

Dye-sensitized solar cell (DSSC) as the most promising candidate for the new-generation photovoltaic device, which has attracted increasing attention due to its great advantages: lower fabrication cost, convenient fabrication based on solution, environmental friendly and versatile design for the dyes [1-4]. In DSSC, the dye is a key component, which plays an important role in determining the light-harvesting efficiency and electron injection efficiency from the photoexcited sensitizer into the conduction band (CB) of semiconductor oxide [5]. During the past decade, tremendous efforts have been made to develop novel dyes with broad absorption spectra [6-15]. However, it is a rigorous challenge to design a dye that absorbs sunlight efficiently from the visible to the near-infrared region, which needs to consider many intricate factors, such as the narrowing of the energy gap of the dye molecules, efficient charge injection and the dye regeneration limit, correspondingly sets a barrier for the design of dye molecules.

In dye molecule development, it is worth noting that there are several classes of dyes possessing strong light responses in their respective regions [6, 7, 16]. Therefore, compared with the development of novel organic dyes, an alternative approach to improve the light-harvesting efficiency is co-sensitization by employing multiple dyes with complementary absorption features sensitized on semiconductor films, extending the light-harvesting ability so as to increase the photocurrents of the devices [17]. As demonstrated, the co-sensitization strategy not only can broaden the spectral response...
range and enhance light-harvesting, but also retard charge recombination on the surface of TiO$_2$, thus making a distinct contribution for improving short-circuit current density ($J_{sc}$) and open-circuit voltage ($V_{oc}$) [18-23].

Herein, we report a promising DSSC based on ruthenium complex dye (N719) co-sensitized with a phenothiazine-based organic dye (PTZ-4). The chemical structure of the used PTZ-4 is depicted in Figure 1. It was found that both $J_{sc}$ and $V_{oc}$ of the co-sensitized DSSC (N719+PTZ-4) were significantly enhanced relative to the single N719 sensitized device, which owing to the co-sensitized DSSC could effectively enhance light-harvesting efficiency and reduce charge recombination.

![Figure 1. Molecular structure, HOMO and LUMO of PTZ-4.](image)

2. Results and discussion

In this study, the co-sensitized anode films were prepared by cocktail approach [26-27]. Since the chosen primary sensitizer N719 has achieved some of the high device efficiencies, the objective of co-sensitization is to further enhance photovoltaic performance by co-adsorbing dye PTZ-4. For comparison, control devices sensitized by individual N719 and PTZ-4 were also fabricated. Figure 2 shows the $J$-$V$ curves of DSSCs based on PTZ-4, N719 and N719 + PTZ-4. $J$-$V$ characteristics were measured under AM1.5 one sun illumination (100mW cm$^{-2}$). Device sensitized with only PTZ-4 showed a $J_{sc}$ of 10.95mA cm$^{-2}$, a $V_{oc}$ of 0.73 V and a FF of 0.65, generating a PCE of 5.14%. At the same time, the N719 sensitized DSSC gave a $J_{sc}$ of 15.80mA cm$^{-2}$, a $V_{oc}$ of 0.71 V and a FF of 0.64, resulted in a PCE of 7.11%. Upon co-sensitization, the performance of the N719 + PTZ-4 device improved to yield $J_{sc}$=16.69mA cm$^{-2}$, $V_{oc}$=0.75V, FF=0.67 and PCE=8.42%. It is noted that the $J_{sc}$ and $V_{oc}$ values are tremendously improved by the co-sensitization of N719 and PTZ-4.

![Figure 2. J-V curves of DSSCs based on single sensitizer or co-sensitizers.](image)
Figure 3. (a) UV-vis absorption spectra of PTZ-4 and N719 in solution; (b) UV-vis spectra of the single PTZ-4, N719 and co-sensitizers anchored onto TiO₂ films; (c) IPCE spectra of DSSCs based on single sensitizer or co-sensitizers.

For the co-sensitized system, the enhancement of $J_{sc}$ owing to more efficient light-harvesting ability, which are understandable from the UV-vis absorption spectra and IPCE spectra. Figure 3a and 3b illustrate the UV-vis absorption spectra of PTZ-4 and N719 in solution and adsorbed on TiO₂ film, respectively. As shown in Figure 3a, the N719 appeared two broad visible bands at 530nm.
respect to single N719 (Figure 3c). However, the defect at this part. Upon co-absorption with PTZ-4, there was nearly no influence on the onset of IPCE with the range of 300-450 nm left a problem to be solved. Notably, the decrease of the IPCE to 40% in the range of 300-450 nm left a problem to be solved. Furthermore, compared with the absorption spectrum of N719 in solution, apparently, the absorption spectrum of PTZ-4 can compensate for that of N719 in the low wavelength region. It is expected that a better light-harvesting ability can be achieved based on the co-sensitized N719 with PTZ-4. After adsorption on TiO$_2$ film (Figure 3b), both PTZ-4 and N719 show an absorption spectrum with broadened spectral response range and dramatic red-shift as compared to their respective absorption spectra of dye solution, which indicates that the dyes of both PTZ-4 and N719 formed $J$-aggregation on TiO$_2$ surface. In addition, it was obvious that when combined N719 with PTZ-4 for the complementary in their spectral responses, its absorption in the region of $\sim$400-530nm on TiO$_2$ film was significantly enhanced when compared with the individually sensitized N719 TiO$_2$ film, which ensures harvesting more sunlight, resulting in impressively improved $J_{sc}$.

The cell sensitized with only N719 had a broad IPCE spectrum across the whole visible range into 800 nm and displayed the high IPCE value (73%) in the wavelength range from 450 to 600 nm (Figure 3c). Notably, the decrease of the IPCE to 40% in the range of 300-450 nm left a problem to be solved in this part. Upon co-absorption with PTZ-4, there was nearly no influence on the onset of IPCE with respect to single N719 (Figure 3c). However, the defect at $\sim$330-530 nm of IPCE spectra was compensated, which was in agreement with their absorption spectra on TiO$_2$ film (Figure 3b). Furthermore, the IPCE spectrum of co-sensitized DSSC almost did not change in the long wavelength region with respect to that of N719-based DSSC. This phenomenon implied that the adsorption of N719 under co-sensitization condition was almost not affected by PTZ-4 [21, 29]. In addition, it can be derived that a better dye coverage on the surface of TiO$_2$ was formed upon co-sensitization from the IPCE spectra [30]. Consequently, the co-sensitized DSSC yielded enhanced light-harvesting efficiency and higher $J_{sc}$ than DSSC based on individual N719.

To account for the enhanced $V_{oc}$ upon co-sensitization and investigate the interfacial charge transfer, recombination processes, EIS was employed under a bias of 0.75 V with a frequency range of $10^2$ Hz to $10^4$ Hz in the dark [31]. The equivalent circuit model has been used to fit the EIS data. As shown in Figure 4a, the semicircle at high frequency is typically considered as charge transfer at Pt electrolyte/counter electrode interface ($R_\alpha$). The main semicircle in the low frequency range is mainly attributed to the resistance of the recombination between electrons on the CB of TiO$_2$ and I$_3$ in the electrolyte ($R_{ct}$). A smaller $R_{ct}$ value means a faster charge recombination rate and a larger dark current, ultimately resulting in a smaller $V_{oc}$. The fitted $R_{ct}$ of PTZ-4, N719 and N719+PTZ-4 is 50, 35.90 and 56.67 $\Omega$, respectively, which indicates that co-sensitization can reduce recombination of injected electron in TiO$_2$ with the I$_3$-aggregation, resulting in larger $V_{oc}$. This tendency of $R_{ct}$ values was consistent with the $V_{oc}$ order of the DSSCs.

In addition, electron lifetime ($\tau_e$) is one of the important factors affecting photovoltage of DSSCs. The $\tau_e$ can be extracted from the peak frequency ($f$) at a lower frequency region in EIS Bode phase plots (Figure 4b) using $\tau_e=1/(2\pi f)$. For the three devices, the $\tau_e$ was enhanced with the calculated values of N719+PTZ-4 (16.17 ms)>PTZ-4 (14.12 ms)>N719 (12.11 ms). Longer $\tau_e$ indicates improved suppression of back reactions between the injected electrons and the electrolyte, which leads to improvement of $V_{oc}$ due to reduced charge recombination rate. So the higher $V_{oc}$ of the co-sensitized DSSC can be further explained.
3. Conclusion
In conclusion, a cocktail approach has been applied for the co-sensitization of ruthenium complex dye (N719) with phenothiazine-based metal free dye (PTZ-4) for DSSC. It was found that the $J_{sc}$ and $V_{oc}$ values of the co-sensitized DSSC (N719+PTZ-4) were significantly enhanced relative to the DSSC sensitized with individual N719, resulting in impressively improved photovoltaic performances. Consequently, the co-sensitized DSSC based on N719 with PTZ-4 gave a PCE of 8.42%, exhibiting an improvement of 18.42% compared to the device sensitized with N719 alone (PCE=7.11%) under the same conditions. The enhancement of the $J_{sc}$ value of the co-sensitized device is ascribed to the improved light-harvesting efficiency. Meanwhile, charge recombination was significantly retarded for the co-sensitized DSSC relative to each individual dye-sensitized system, to account for the enhanced $V_{oc}$. We hope the present work can provide guidance, with appropriate molecular design, to seek more promising co-sensitized solar cells with the ability to harvest an increased portion of the solar spectrum and reduce charge recombination.

References
[1] B. O'Regan, M. Grätzel, Nature 353 (1991) 737.
[2] S. Zhang, X. Yang, Y. Numata, et al., Energy Environ. Sci. 6 (2013) 1443.
[3] A. Mishra, M.K. Fischer, P. Bauerle, Angew. Chem. Int. Ed. 48 (2009) 2474.
[4] A. Hagfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49.
[5] A. Hagfeldt, G. Boschloo, L. Sun, et al., Chem. Rev. 110 (2010) 6595.
[6] S. Mathew, A. Yella, P. Gao, et al., Nat. Chem. 6 (2014) 242.
[7] C. Chen, M. Wang, J. Li, et al., ACS Nano 3 (2009) 3103.
[8] S. Fernandes, M. Castro, I. Mesquita, et al., Dyes Pigments 136 (2017) 46.
[9] S. Manoharan, A.M. Asiri, S. Anandan, Solar Energy 126 (2016) 22.
[10] S. Manoharan, J.J. Wu, S. Anandan, Dyes Pigments 133 (2016) 222.
[11] Z. Yao, M. Zhang, H. Wu, et al., J. Am. Chem. Soc. 137 (2015) 3799.
[12] H. Vu, T. Atabaev, D. Pham-Cong, et al., Electrochim. Acta 193 (2016) 166.
[13] W. He, T.S. Atabaev, H.K. Kim, et al., J. Phys. Chem. C 117 (2013) 17894.
[14] F. Iradi, D. O’Neil, X. Kang, et al., Chem. Mater. 27 (2015) 6305.
[15] C. Qin, Y. Numata, S. Zhang, et al., Adv. Funct. Mater. 24 (2014) 3059.
[16] Z.-S. Wang, H. Kawachi, T. Kashima, et al., Chem. Rev. 248 (2004) 1381.
[17] C. Lan, H. Wu, T. Pan, et al., Energy Environ. Sci. 5 (2012) 6460.
[18] C. Qin, Y. Numata, S. Zhang, et al., Adv. Funct. Mater. 23 (2013) 3782.
[19] J. Luo, Z. Wan, C. Jia, et al., Electrochim. Acta 215 (2016) 506.
[20] R. Yan, X. Qian, Y. Jiang, et al., Dyes Pigments 141 (2017) 93.
[21] L. Han, A. Islam, H. Chen, et al., Energy Environ. Sci. 5 (2012) 6057.
[22] A. Yella, H. Lee, H. Tsao, et al., Science 334 (2011) 629.
[23] K. Kakiage, Y. Aoyama, T. Yano, et al., Chem. Commun. 51 (2015) 15894.
[24] J. Luo, Z. Wan, C. Jia, Chin. Chem. Lett. 27 (2016) 1304.
[25] J. Luo, Z. Wan, C. Jia, et al., Electrochim. Acta 211 (2016) 364.
[26] Y. Chen, Z. Zeng, C. Li, et al., New J. Chem. 29 (2005) 773.
[27] J.N. Clifford, A. Forneli, H. Chen, et al., J. Mater. Chem. 21 (2011) 1693.
[28] Z. Wu, Y. Wei, Z. An, et al., Korean Chem. Soc. 35 (2014) 1449.
[29] M. Kimura, H. Nomoto, et al., Angew. Chem. Int. Ed. 51 (2012) 4371.
[30] S. Singh, M. Chandrasekharam, K. Gupta, et al., Org. Electron. 14 (2013) 1237.
[31] F. Santiago, J. Bisquert, L. Cevey, et al., J. Am. Chem. Soc. 131 (2009) 558.