

Research Article

Effect of Deoxycholic Acid on the Performance of Liquid Electrolyte Dye-Sensitized Solar Cells Using a Perylene Monoimide Derivative

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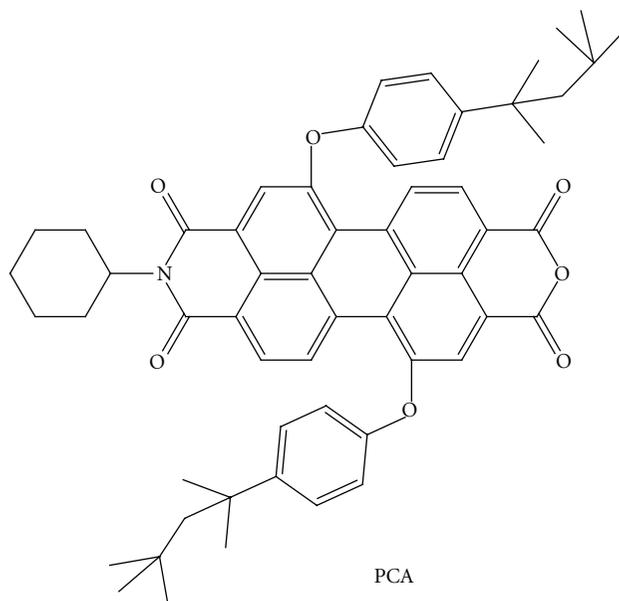
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The effect of coadsorption with deoxycholic acid (DCA) on the performance of dye-sensitized solar cell based on perylene monoimide derivative (PCA) as sensitizer and liquid electrolyte had been investigated. The current-voltage characteristics under illumination and incident photon to current efficiency (IPCE) spectra of the DSSCs showed that the coadsorption of DCA with the PCA dye results in a significant improvement in short circuit photocurrent and slight increase in the open circuit photovoltage, which lead to an overall power conversion efficiency. The enhancement of short circuit current was attributed to the increased electron injection efficiency from the excited state of PCA into the conduction band of TiO₂ and charge collection efficiency. The current-voltage characteristics in dark indicates a positive shift in the conduction which also supports the enhancement in the photocurrent. The coadsorption with DCA suppressed charge recombination as indicated from the electrochemical impedance spectra and thus improved the open circuit photovoltage.

1. Introduction

Dye-sensitized solar cells (DSSCs) represent one of the most promising candidates for developing new renewable energy sources due to their low cost and high efficiency [1–6]. Typical DSSCs consist of a dyed semiconductor TiO₂ photoelectrode, a Pt counterelectrode, and redox electrolyte. Among these components, the sensitizer, that is, dye, is one of the key components that affects the overall power conversion efficiency (PCE) of the DSSC. The dye must absorb sunlight over a wide region of visible and near infrared (NIR) and inject the photoexcited electrons into the conduction band of the semiconductor in the photoelectrode. The typical dyes at present times are Ruthenium-based dyes, such as N3, N719,

and black dye have achieved PCEs up to 11%, due to their intense and wide range absorption of visible light [7–10]. However, due to the relatively high cost and environmental concerns associated with the use of Ru-based dyes have inspired strenuous efforts to develop metal-free dyes as the alternative sensitizers [11–14]. Moreover, high molar extinction coefficients of metal-free dyes allow the use of thinner TiO₂ film, which is beneficial for charge separation [15, 16]. Another important advantage over Ru-based dyes is the availability of versatile functional molecules associated with tuning the electronic and optical properties. Recently, the DSSCs performance based on organic dye has been remarkably improved and reached impressive PCE more than 9% [15] and 11% by porphyrin dyes [17, 18].



SCHEME 1: Chemical structure of perylene monoimide derivative PCA.

Perylene dyes are well known as the key chromophores among the metal-free dyes [19–26]. Their solubility, absorption, and emission behavior can be efficiently controlled using a variety of synthetic procedures, which include functionalization of *peri*- or *bay*-positions of perylene core. Moreover due to their outstanding photophysical and photochemical stability as well as their high fluorescence quantum yields, perylene derivatives have been used as active components for application in organic electronic devices [27–35]. Systematic tuning of HOMO and LUMO levels of perylene dyes improve both light harvesting properties and electron injection capabilities to TiO_2 conduction band for obtaining the high PCE. Several perylene dyes have been used as sensitizers in DSSCs [36–45]. Edvinsson et al. reported that by attaching a bulky nonplanar di-*p-tert*-octylphenylamino and an anhydride moiety to the perylene core, which not only suppresses the aggregation of dye molecules but also improves the stability of the organic sensitizer [46]. With two additional phenylthio groups in the 1,6-positions of the perylene unit, a new perylene sensitizer yields 87% incident monochromatic photon-to-current conversion efficiency (IPCE) and 6.8% power conversion efficiency under standard AM 1.5 solar conditions [47].

Another strategy for enhancing the PCE is to incorporate donor-linker-acceptor (D- π -A) into the framework. Introducing D- π -A groups increases intramolecular charge transfer from donor to acceptor side of the molecule by π linker, which results a strong electron transfer from excited state of dye molecule to the conduction band of TiO_2 .

In the present paper, perylene monoimide (PCA) has been employed as sensitizer for nanocrystalline TiO_2 DSSC. PCA contains an electron-donating cyclohexyl ring, which is connected with perylene core act as electron acceptor via imide nitrogen. Moreover, PCA carries bulky alkylphenoxy groups at the 1,7 bay positions of perylene core, the alkyl

chains of which enhance the solubility of the compound. Finally, PCA contains an acid anhydride as anchoring group for TiO_2 surface. We have used PCA as sensitizer for the DSSC based on TiO_2 nanocrystalline photoanode and liquid electrolyte. The effect of deoxycholic acid (DCA) as coadsorbent on the photovoltaic performance of DSSCs based on PCA had been investigated. The improvement in the overall PCE is attributed to enhancement in both J_{sc} and V_{oc} . The enhancement in the J_{sc} of DSSC upon the DCA coadsorption was attributed to the increased efficiency of electron injection and/or charge collection efficiency. The coadsorption of DCA suppressed charge recombination and thus improved V_{oc} .

2. Experimental Part

The synthesis of PCA has been reported by us in our earlier communication [48]. The chemical structure of the PCA is shown in Scheme 1. The UV-visible absorption spectra of the dye-loaded TiO_2 film was recorded on a Shimadzu UV-visible spectrophotometer. The cyclic voltammograms were measured with a three electrode electrochemical cell on potentiostat/Galvanostat PGSTAT30 electrochemical analyzer. The dye-loaded TiO_2 film, platinum and Ag/Ag^+ (0.01 M AgNO_3 + 0.1 MTBAP in acetonitrile) were employed as working, counter, and reference electrodes, respectively. The supporting electrolyte was 0.1 M LiClO_4 in acetonitrile. The potential of the reference electrode is 0.49 V versus normal hydrogen electrode (NHE) and is calibrated with ferrocene immediately after cyclic voltammogram measurement.

TiO_2 paste was prepared by mixing 1 g of TiO_2 powder (P_{25} , Degussa), 0.2 mL of acetic acid, 1 mL of water. Then 60 mL of ethanol was slowly added while sonicating the mixture for 3 h. Finally, Triton X-100 was added and a well-dispersed colloidal paste was obtained (TiO_2). The whole

procedure is slow under vigorous stirring. The mixture was stirred vigorously for 2–4 h at room temperature and then stirred for 4 h at 100°C to form a transparent colloidal paste. The TiO₂ paste was deposited on the F-doped tin oxide- (FTO-) coated glass substrates by the doctor blade technique. The TiO₂ coated FTO films were sintered at 450°C for 30 min. After cooling to room temperature, the electrodes were impregnated in 0.05 M titanium tetrachloride aqueous solution, washed with distilled water, and again sintered at 450°C for 30 min followed by cooling to room temperature. The thickness of the TiO₂ layer is about 12 μm. PCA dye solutions (0.5 mM) with and without DCA (10 mM) were prepared in THF and used to sensitize the TiO₂ electrodes by immersing the TiO₂ films in these dye solution for 24 h and then washed.

A thin Pt layer was deposited on an FTO conducting glass by thermal pyrolysis of H₂PtCl₄ in isopropanol solution and then heated at 450°C for 30 min in air. One drop of electrolyte solution (0.6 M 1-propyl-2,3 dimethyl-imidazolium iodide DMPImI, 0.1 M LiI, 0.05 M iodine, and 0.5 M tetrabutyl pyridine in acetonitrile) was deposited onto the surface of dye-sensitized TiO₂ electrode and penetrated inside the TiO₂ via capillary action. The Pt-coated FTO electrode was then clipped onto the top of TiO₂ working electrode to form the complete DSSC. The active area of each DSSC thus prepared was about 0.4 cm².

The current-voltage characteristics of DSSCs were measured on a computer controlled source meter (Keithley, 2400). An AM 1.5 solar simulator with 150 W xenon lamp and an AM filter were used as the light source. Light intensity corresponding to AM 1.5 (100 mW/cm²) was calibrated using a standard silicon solar cell. Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a monochromator system. The output current under short circuit condition at each wavelength was measured using the Keithley electrometer.

Electrochemical impedance spectra for DSSCs in dark and under illumination were measured with electrochemical analyzer, equipped with FRA software. The spectra were scanned in the frequency range of 0.01–10⁵ Hz at room temperature with applied potential set at open circuit voltage. The magnitude of modulation signal was set at 20 mV.

3. Results and Discussion

Figure 1 depicts the optical absorption spectra of the PCA in THF solution and PCA adsorbed into the TiO₂ nanocrystalline film. The absorption curve in solution shows an optical absorption maximum around 510 nm and is broad extended up to 680 nm. Therefore the PCA exhibits very nice absorption coverage over the visible and near infrared (NIR) region, which is desirable for the photovoltaic application. The absorption onset is located around 645 nm that corresponds to an optical band gap around 1.92 eV.

When PCA dye was sensitized on TiO₂ surface, the absorption maxima was redshifted by about 20 nm in comparison to those in solution (Figure 1), due to the *J* aggregation on the semiconductor surface [23, 49].

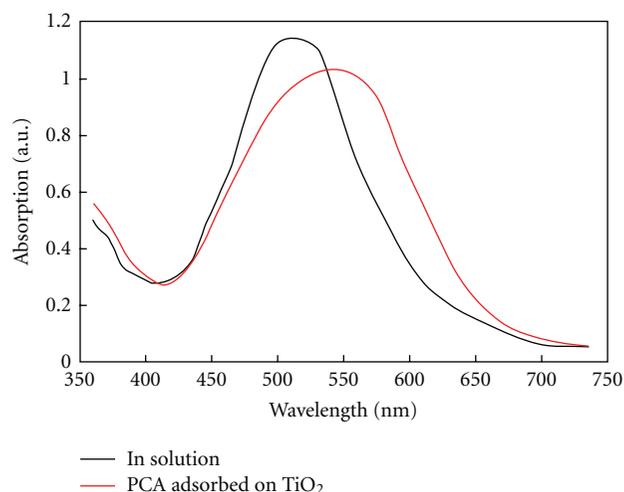


FIGURE 1: Optical absorption spectra of PCA in THF solution and adsorbed on TiO₂ nanocrystalline thin film.

To evaluate the possibility of electron injection occurring from the excited state of dye molecules to the conduction band of TiO₂, the electrochemical oxidation and reduction potentials of the dyes were measured by cyclic voltammetry (CV) using three electrode cells.

The oxidation potential of the ground state of PCA, which corresponds to their HOMO level is 1.05 V versus NHE. This value is sufficiently more positive than the I^-/I_3^- redox potential (0.4 V versus NHE) and indicates that the oxidized PCA formed after the injection of electrons into the conduction band of TiO₂ could accept the electrons from I^- ions thermodynamically. The reduction potential of PCA dye, which corresponds to their LUMO level is -0.95 V versus NHE, which is more negative than the TiO₂ conduction band edge (-0.5 V versus NHE). The energy gap between the LUMO level of PCA and the conduction band level of TiO₂ is 0.45 V. Since the energy gap of around 0.2 V is necessary for efficient electron injection [50], the energy gap values of the dyes were above this value indicates that the excited electrons of the dye molecule can be injected into the conduction band of TiO₂ thermodynamically.

The current-voltage characteristics of the DSSCs based on PCA with and without DCA was measured at 100 mW/cm² and shown in Figure 2(a). The photovoltaic parameters are compiled in Table 1. The DSSC based on PCA without DCA coadsorbent gave a J_{sc} of 8.7 mA/cm², V_{oc} of 0.63 V, and an FF of 0.56, corresponding to overall PCE of 3.07%. Under the same conditions, when DCA is incorporated into the dye solution, the DSSC showed a J_{sc} of 10.8 mA/cm², V_{oc} of 0.68, and FF of 0.61, resulting an overall PCE of 4.48%.

Figure 2(b) compares the photocurrent action spectra of the DSSCs before and after coadsorption with DCA, where incident photon to current efficiency (IPCE) is plotted as a function of wavelength. The IPCE values of DSSC based on PCA with DCA are higher than those for PCA without DCA, in the whole wavelength region. Because IPCE is a product of electron injection efficiency, light harvesting efficiency, and

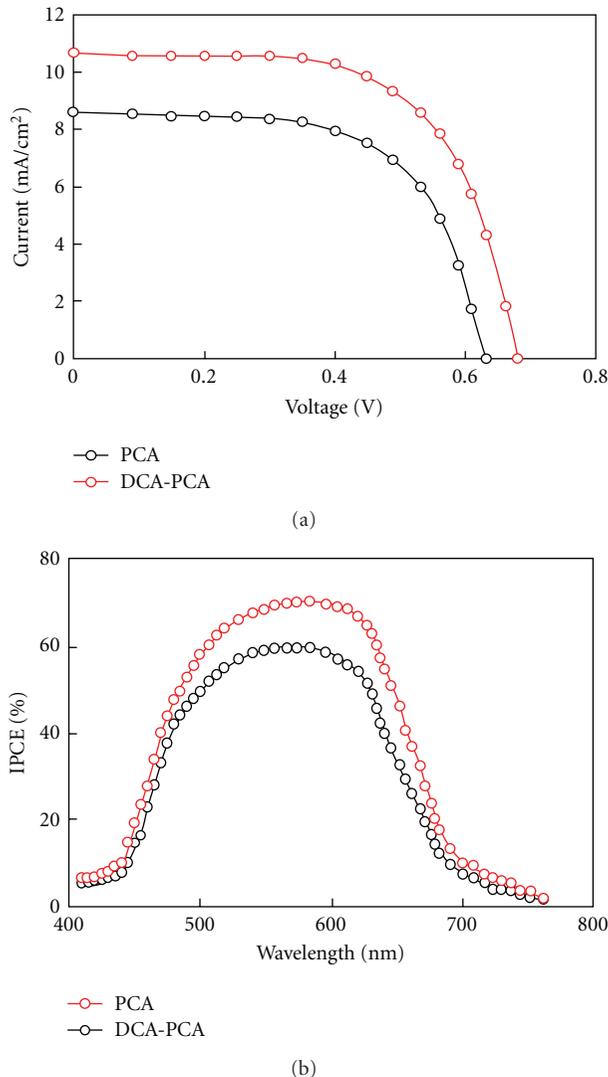


FIGURE 2: (a) Current-voltage characteristics under illumination and (b) IPCE spectra of the DSSCs based on PCA sensitizer with and without DCA coadsorbent.

charge collection efficiency, it is interesting to analyze which factor affects IPCE and J_{sc} . We have estimated the amount of adsorbed dye on the TiO₂ surface by desorbing the dye with basic solution and found that the surface concentration of PCA with and without DCA is about 4.6×10^{-7} and 1.5×10^{-7} mol/cm², respectively. Upon coadsorption with DCA, although the amount of dye adsorbed on the TiO₂ surface is reduced, the IPCE spectra become broader with maximum IPCE improved from 60% to 71%. It is observed that the dye loading reduced on the coadsorption, resulted the reduction in LHE. Therefore, the IPCE improvement is attributed to the enhancements of electron injection efficiency and charge collection efficiency.

It has been already reported in literature that upon coadsorption with DCA, the TiO₂ surface is protonated and conduction band edge shifts positively due to the proton adsorption [12, 50, 51]. This positive shift of conduction

TABLE 1: Photovoltaic parameters of DSSCs based on PCA with and without DCA coadsorbent.

Dye	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
PCA	8.7	0.63	0.56	3.07
DCA-PCA	10.8	0.68	0.61	4.48

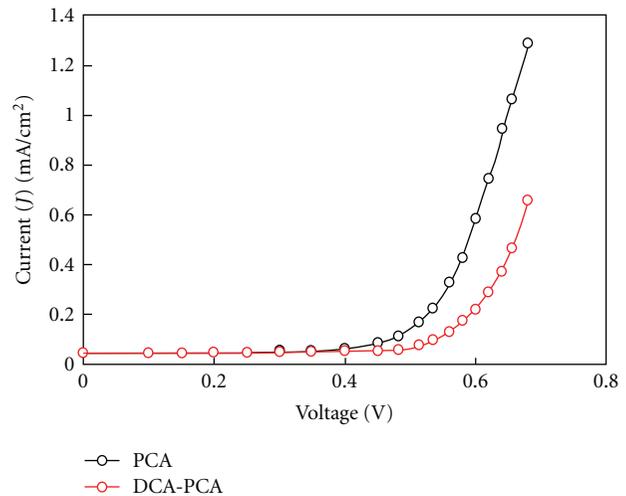


FIGURE 3: Dark current-voltage characteristics of DSSCs based on PCA with and without DCA.

band enlarge the driving force for electron injection from the excited state of dye into the conduction band of TiO₂ which results in the values of IPCE and J_{sc} . In addition, coadsorption can break up the dye aggregation, and the nonaggregated dye molecules are favorable for electron injection.

In DSSC the value of V_{oc} is theoretically the difference between the Fermi level of TiO₂ under light and the redox potential of the redox couple I^-/I_3^- , the positive shift of conduction band edge upon coadsorption with DCA will result in a decrease in V_{oc} . However, we have observed a slight increase in the V_{oc} after coadsorption with DCA that is attributed to the suppression of charge recombination. To understand the role of DCA in improving performance parameters, effect of DCA on dark current was studied as shown in Figure 3. It is observed that the dark current onset potential shifted to a larger value, and also the dark current was also reduced upon the DCA adsorption. The addition of DCA in the dye solution, the surface properties of TiO₂ nanoparticle thin film layer by the passivation effect had similar result as also reported by De La Graza et al. for the modified TiO₂ layer by enediol ligands [52]. This effect of surface states leads to shifts the flat band potential and to decrease the charge recombination. The shift of the onset potential of dark current (Figure 3), in the presence of DCA in the dye solution, can also reflect less participation of surface state in the charge transfer and leads to suppression of charge recombination between the injected electrons and I_3^- ions in the electrolyte, favorable for improvement in V_{oc} . The enhancement of V_{oc} is usually associated with the negative shift on conduction band edge or suppression of

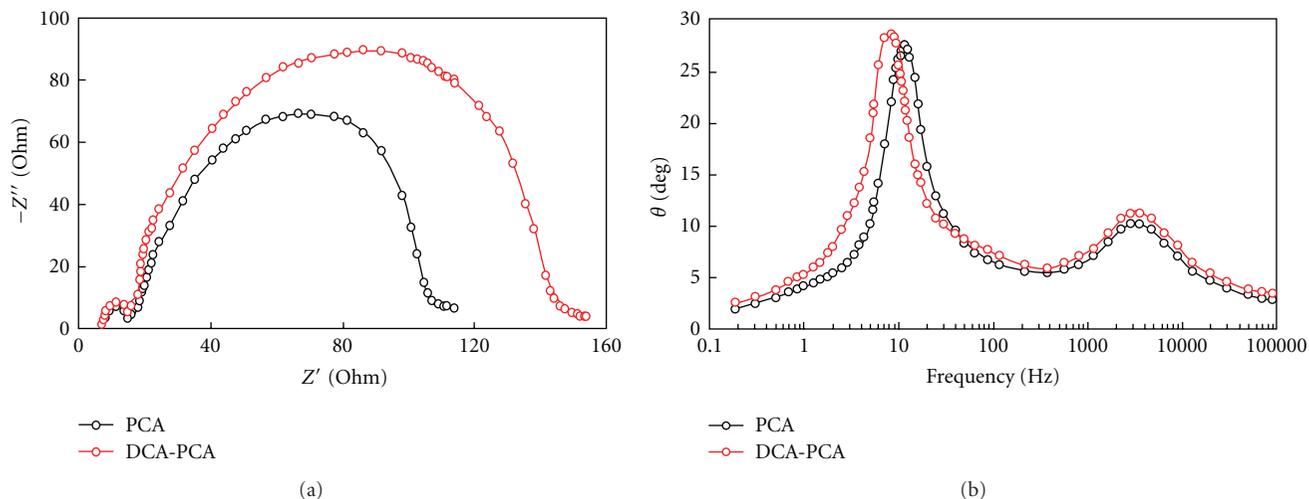


FIGURE 4: Electrochemical impedance spectra (EIS) of DSSCs based on PCA with and without DCA coadsorbent (a) Nyquist plots, (b) Bode phase plots.

charge recombination. Consequently, suppression of charge recombination may compensate for the V_{oc} loss because of proton exchange from DCA to the TiO_2 surface, resulting in V_{oc} improvement.

To further classify the DCA effect on the photovoltaic parameters, electrochemical impedance spectrum (EIS), which is a powerful tool to elucidate the electronic and ionic transport processes in DSSCs was measured in dark under a forward bias of -0.65 V. Three semicircles were observed in the Nyquist plots (Figure 4(a)). The large semicircle in the Nyquist plots located in the middle is attributed to the dark reaction impedance caused by charge transportation at the TiO_2 /dye/electrolyte interface, and other two small semicircles located in the low and high frequency regions are assigned to the charge transfer at counter electrode and diffusion of I_3^- in the electrolyte, respectively [12, 52–55]. It can be seen from Figure 4(a) that the radius of the semicircle in middle frequency region is larger for the DSSC based on DCA coadsorbent PCA than that for PCA only, indicating that the electron recombination resistance is higher for former than that for latter. The higher charge recombination resistance observed for the DSSC with DCA coadsorbent also indicated that there exists efficient suppression of back reaction of injected electron with I_3^- ions in the electrode, which is reflected from the improvement in the both V_{oc} and J_{sc} , yielding substantially enhanced overall power conversion efficiency. The electron lifetime derived from the Bode plots of EIS spectra (Figure 4(b)) is 12.7 ms and 18.3 ms for PCA- and DCA-PCA-based DSSCs, respectively. The longer electron lifetime in the TiO_2 film for the DSSCs sensitized with DCA coadsorbent as compared to that for with DCA also supports the higher value of IPCE and PCE.

4. Conclusion

We have investigated the photovoltaic response of the DSSC based on PCA dye using TiO_2 nanocrystalline TiO_2

photoanode and liquid electrolyte and achieved overall PCE of about 3.07%. The effect of coadsorption of the DCA on the photovoltaic performance of DSSC based on PCA dye was also studied. We found that DCA improves both J_{sc} and V_{oc} . As a consequence, overall efficiency has been enhanced up to 4.48%.

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