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Acid azo dyes for efficient molecular photovoltaic: study of dye-sensitized solar cells performance

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ABSTRACT

In this paper we sensitized three free-metal azo dyes (Dye 1, Dye 2 and Dye 3) based on 1,8-naphthalimide with n-propyl as the electron donor group. We used sulfonic acid and hydroxyl substituents as the electron acceptor anchoring group in synthesized dyes. The proposed dyes were synthesized from acenaphthene as the starting material by standard reactions and characterized by different techniques such as melting point, FT-IR, ^{1}HNMR, elemental analysis and UV-Visible spectroscopy after purification. Spectrophotometric measurements of the azo dyes in solution and on a TiO_2 substrate were carried out in order to assess changes in the status of the dyes. The wavelength of maximum absorption for Dye1, Dye 2 and Dye 3 in solution is 530 nm, 568 nm and 550 nm and on TiO_2 films are 552 nm, 591 nm and 575 nm, respectively. Finally, the proposed dyes used as sensitizer in a dye solar cell structure and their photovoltaic properties were investigated. The Conversion efficiency for Dye 1, Dye 2 and Dye 3 are 2.11% and 2.32% and 2.17%, respectively. Prog. Color Colorants Coat. 9 (2016), 61-70 © Institute for Color Science and Technology.

1. Introduction

Dye-sensitized solar cells (DSSCs) or Gratzel Cells have attracted board attentions, as they offer high energy conversion efficiencies due to low cost and being environmentally friendly [1]. Recently, all over the world are beginning to the application of metal-free organic dyes in dye-sensitized solar cells because such organic dyes do not contain limited-resource expensive ruthenium, and have additionally the advantage of relatively easy production and good reproducibility [2]. To date, various high performance organic dyes have been synthesized, most of which are coumarine [3], polyene [4], hemicyanine [5], thiophene based [6], and indoline [7] dyes. In such photovoltaic materials, the electron-donating and electron-accepting groups are

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connected through a π-conjugated linker (a D-π-A molecular structure) [8]. Their photovoltaic properties can be finely tuned by independently altering, alternating or matching different inorganic dyes groups [9]. In research for high power conversion efficiency organic dyes for dye-sensitized solar cells, development of new substituents and materials offering optimized mechanical stabilities, as well as appropriate optical and electrical properties is of utmost importance [10, 11]. There is few study about application zao dyes performance in dye-sensitized solar cells. Mahmood et al. presented a series of azo dyes for DSSCs. The results show that all azo dyes are suitable for dye-sensitized solar cells and high photo-voltage of 1.128 eV has been achieved [12]. There are several papers on the application of azo dye in new technologies as sensors [13-15] but, there isn't any report on application of acid azo dyes in DSSCs.

In the present study, three metal-free organic dyes were synthesized utilizing n-propyle as the electron donor and sulfonic acid and hydroxy as the electron acceptor groups. The dyes together with their corresponding intermediates were then purified and characterized. The spectrophotometric properties of the synthesized azo dyes in DMF solvent and on the nanoanatase TiO_2 substrate were examined. The absorption maxima and the intensities of the resultant dyes were also obtained. Dye sensitized solar cells were then fabricated utilizing these metal-free organic dyes and their photovoltaic behaviors were characterized. Schematic representation of the route for synthesis of the prepared metal-free organic dyes is given in Figure 1.

2. Experimental

2.1. Materials and instrumentation

All compounds used in this study were of analytical grade unless otherwise stated. The synthesis route and fully characterization of intermediates (1) have been described previously [16]. The FT-IR measurements were carried out on a Bomene Canada instrument. NMR measurements were carried out on a 500MHz Joel instrument. Differential scanning calorimetric (DSC) analyses were carried out on a Dupont 2000DSC instrument. UV-visible spectrophotometry was carried out on a Cecil 9200 double beam transmission spectrophotometer to obtain molar extinction coefficients and absorption maxima.

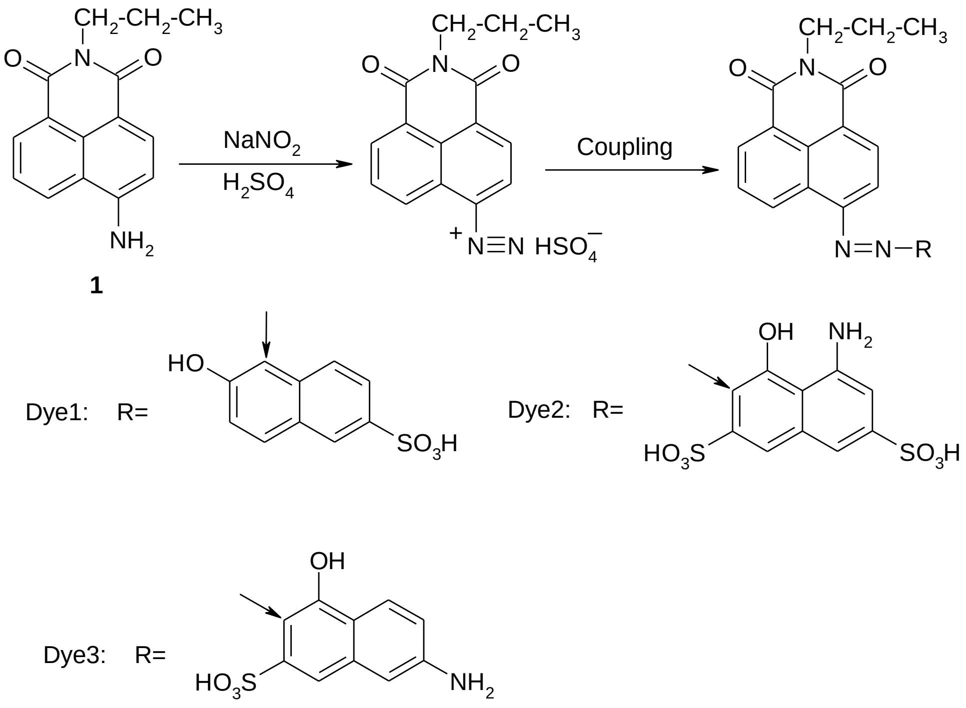


Figure 1: Synthesis route of the dyes.

2.2. Synthesis of Dyes

2.2.1. Synthesis of Dye 1

The method of diazotization was as follows: 3.5 mL sulfuric acid (98 %) was cooled to below 10 °C and 0.13 g (2 mmol) sodium nitrite was added with stirring in a 20 min period and the stirring continued for a further 10 min, after which the temperature was gradually increased to 65 °C until all the sodium nitrite was dissolved. The solution was then cooled to below 10 °C and 2 mmol 4-amino-N-propyl-1,8-naphthalimide was added gradually over a 0.5 h period. Temperature was kept below 10 °C. This was followed by the addition of 1 mL glacial acetic acid over a 10 min period to the reaction mixture. The mixture was stirred for a further 3 h at below 10 °C and the final diazonium salt was prepared. 2 mmol of Schaeffer's acid was dissolved in 8.5 mol ethanol to which the diazonium salt was added gradually over a 25 min period while the temperature was kept below 10 °C. The mixture was stirred for 3 h and was filtered followed by washing with hot water and drying.The resultant precipitate was filtered and purified by silica gel column chromatography (DMF: H_2O, 1:1). Yield: 89%; mp250.7 °C; FT-IR (KBr) (Cm^{-1}): 1657 C=O str., 1482, 1609: C=C str, 1498: C-N str; ^{1}H-NMR ($CDCl_3$), δ (ppm): 0.93-1.01(3H, N-$CH_2CH_2\underline{CH_3}$), 1.76-1.80 (2H, N-$CH_2\underline{CH_2}CH_3$), 3.47-3.51 (2H, N-$\underline{CH_2}CH_2CH_3$), 7.38-7.47 (d, 2H), 7.57 (t, H), 7.71-7.73 (d, 2H), 8.10-8.12 (d, 2H), 8.22-8.33 (d, 2H), 8.34-8.61 (d, 1H), 16.60 (s, 1H, OH); ^{13}CNMR ($CDCl_3$, δ/ppm): 50.78, 55.34, 59.41, 109.13, 115.77, 116.11, 117.22, 120.07, 120.91, 121.42, 122.45, 123.31, 124.16, 125.71, 126.74, 127.15, 128.61, 129.41, 129.85, 130.24, 131.12, 133.28, 135.31, 137.11, 139.12, 141.17, 142.37, 165.44; Elem. Anal. Calcd. for $C_{25}H_{19}N_3O_6S$: C, 61.34%; H, 3.88%; N, 8.58%. Found: C, 61.28%; H, 3.72%; N, 8.47%.

2.2.2. Synthesis of Dye 2

The method of diazotization was as follows: 3.5 mL sulfuric acid (98 %) was cooled to below 5 °C and 0.13 g (2 mmol) sodium nitrite was added with stirring in a 20 min period and the stirring continued for a further 10 min, after which the temperature was gradually increased to 65 °C, until all the sodium nitrite was dissolved. The solution was then cooled to below 10 °C and 2 mmol 4-amino-N-propyl-1,8-naphthalimide was added gradually over a 30 min period. Temperature was kept below 5 °C. This was followed by the addition of 1 mL glacial acetic acid over a 10 min period to the reaction mixture. The mixture was stirred for a further 3 h at below 5 °C and the final diazonium salt was prepared. 2 mmol of H-acid was dissolved in 10 mol ethanol to which the diazonium salt was added gradually over a 30 min period, the temperature was kept below 5°C. The mixture was stirred for 3 h and was filtered followed by washing with hot water and drying. The resultant precipitate was filtered and purified by silica gel column chromatography (DMF: H_2O, 1:1). Yield: 87%; mp279.43 °C; FT-IR (KBr) (Cm^{-1}): 1703 C=O str., 1471, 1607: C=C str, 1403: C-N str; ^{1}H-NMR ($CDCl_3$), δ (ppm): 0.98-1.06(3H, N-$CH_2CH_2\underline{CH_3}$), 1.66-1.74 (2H, N-$CH_2\underline{CH_2}CH_3$), 3.55-3.59 (2H, N-$\underline{CH_2}CH_2CH_3$), 7.39 (s, 2H), 7.59 (t, H), 7.72 (2H, NH_2), 8.11-8.16 (d, 2H), 8.29-8.34 (s, 2H), 8.41-8.46 (d, 1H), 16.79 (s, 1H, OH);^{13}C-NMR ($CDCl_3$, δ/ppm): 50.44, 55.11, 63.77, 110.34, 112.32, 113.29, 119.87, 120.11, 121.16, 124.77, 125.15, 126.72, 127.11, 128.19, 129.49, 130.13, 131.47, 132.42, 133.16, 134.49, 135.19, 137.16, 140.44, 142.41, 148.35, 165.44;Elem. Anal. Calcd. for $C_{25}H_{20}N_4O_9S_2$: C, 51.36%; H, 3.42%; N, 9.58%. Found: C, 52.77%; H, 3.41%; N, 9.72%.

2.2.3. Synthesis of Dye 3

The method of diazotization was as follows: 3.5 mL sulfuric acid (98 %) was cooled to below 10 °C and 0.13 g (2 mmol) sodium nitrite was added with stirring in a 20 min period and the stirring continued for a further 10 min, after which the temperature was gradually increased to 65 °C, until all the sodium nitrite was dissolved. The solution was then cooled to below 10 °C and 2 mmol 4-amino-N-propyl-1,8-naphthalimide was added gradually over a 30 min period. Temperature being kept below 5 °C. This was followed by the addition of 1 mL glacial acetic acid over a 10 min period to the reaction mixture. The mixture was stirred for a further 3 h at below 5 °C and the final diazonium salt was prepared. 2.5 mmol of J-acid was dissolved in 10 mol ethanol to which the diazonium salt was added gradually over a 30 min period, the temperature was kept below 10°C. The mixture was stirred for 3 h and was filtered followed by washing with hot water and drying.The resultant precipitate was filtered and purified by silica gel column chromatography (DMF: H_2O, 1:1). Yield: 92%; mp254.11 °C; FT-IR (KBr) (Cm^{-1}): 1687 C=O str., 1465, 1616: C=C str, 1411: C-N str; ^1H-NMR ($CDCl_3$), δ (ppm): 1.03-1.09(3H, N-$CH_2CH_2\underline{CH_3}$), 1.75-1.79 (2H, N-$CH_2\underline{CH_2}CH_3$), 3.72-3.78 (2H, N-$\underline{CH_2}CH_2CH_3$), 6.75-6.79 (d, 1H), 6.88 (2H, NH_2), 7.26-7.30 (d, 2H), 7.77 (t, 1H), 7.88-7.95 (d, 2H), 8.11-8.16 (d, 2H), 8.26-8.31 (d, 1H), 16.62 (s, 1H, OH);^{13}C-NMR ($CDCl_3$, δ/ppm): 52.34, 54.17, 60.32, 110.11, 111.19, 112.67, 114.63, 116.90, 119.14, 121.43, 122.77, 124.32, 125.19, 126.49, 128.17, 129.44, 131.63, 131.92, 132.88, 133.44, 134.77, 135.46, 136.62, 139.77, 140.44, 167.38;Elem. Anal. Calcd. for $C_{25}H_{20}N_4O_6S$: C, 59.52%; H, 3.96%; N, 11.11%. Found: C, 59.61%; H, 4.03%; N, 11.19%.

2.3. Electrochemical measurements

Electrochemical measurements of the synthesized dyes were carried out in solution in acetonitrile. The oxidation potential (E_{ox}) was measured using three small-sized electrodes. Ag quasi reference electrode (QRE) was used as the reference. Platinum wires were used as the working and the counter electrodes. All electrode potentials were calibrated with respect to ferrocene (Fc)/ferrocenium (Fc^+) redox couplet. An acetonitrile solution of each dye containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) and ferrocene (ca. 1 mmol dm^{-3}) was prepared. The electrochemical measurements were performed at a scan rate of 100 mV s^{-1}[17].

2.4.Dye-sensitized solar cells (DSSCs) assembly and photovoltaic characteristics of the resultant solar cells

A nanocrystalline TiO_2 film was coated on a transparent glass support. The dye was adsorbed by dipping the coated glass in a 5×10^{-5} M ethanolic solution of the dye containing 7% 4-tert-butylpyridine and 50 mM 3α,7α-dihydroxy-5β-cholic acid (cheno) for several hours. The visible bands in the absorption spectrum of the dyes after adsorption on the nano TiO_2 film only appeared after the TiO_2 electrodes were dipped in the dye solution for at least 18 hr. The presence of 4-tert-butylpyridine and cheno is necessary to avoid surface aggregation of the sensitizer (Dye 1, Dye 2 and Dye 3). Finally, the film was washed with an acetonitrile-ethanol 1:1 mixed solution. Acenonitrile-ethylene carbonate (v/v=1:4) containing tetrabutyl ammonium iodide (0.5 mol dm^{-3}) was used as the electrolyte. The dye-adsorbed TiO_2 electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich type solar cell [18-20].

An action spectrum was measured under monochromatic light with a constant photon number (5×10^{15} photon cm^{-2} s^{-1}). J-V characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm^{-2}) through a shading mast (5.0 mm×4 mm) by using a Bunko-Keiki CEP-2000 system.

3. Results and Discussion

Preparation of 4-amino-N-substituted-1,8-naphthalimide as an intermediate plays an important role in the synthesis of naphthalimide acid dyes. The naphthalimides with an amino substituents at the 4-position are also fluorescent emission [21]. 4-Amino-N-substituted-1,8-naphthalimides were obtained by the reaction of 4-nitro-N-substituted-1,8-naphthalimides with tin(II) chloride as the reducing agent and hydrochloric acid as the solvent. Diazotization of naphthalimides derivatives were obtained with the aid of nitrosylsulfuric acid, the procedure being the dissolution of sodium nitrite in concentrated sulfuric acid followed by slow addition of the given amine to the prepared nitrosylsulfuric acid at below 5-10 °C until the diazonium salt was prepared [22, 23]. The reaction was completed in 3 h. Then diazonium salts were reacted with various coupling component such as Schaeffer's acid, H-acid and J-acid in alkaline media (pH ~ 9) (Figure 1).

The wavelength of maximum absorption (λ_{max}) and the molar extinction coefficients (ε_{max}) for the synthesis dyes in DMF:H_2O=1:1 are listed in Table 1 and shown in Figure 2, together with the λ_{max} of the corresponding dyes adsorbed on the TiO_2 film. The absorption peaks at around 530nm for Dye 1 can be assigned to an intra-molecular charge transfer between the donor group and acceptor group [24], providing an efficient charge-separation for the excited state. For the Dye 2, when an extra electron acceptor (sulfonic acid) was linked to the vinyl bridge, the λmax had a bathochromic shift from 530 nm for Dye 1 to 563 nm for Dye 2. This shift of the maximum absorption peak arises from the fact that more stronger electron acceptor of two acceptor groups intensifies the overall electron withdrawing ability of the system and hence lowering the level of the lower unoccupied molecular orbital (LUMO), thus reducing the gap between the higher unoccupied molecular orbital (HOMO) and the LUMO states [2, 25]. The wavelength of maximum absorption has been achieved around 550 nm for Dye 3. Upon dye adsorption on to a photo-anode surface (TiO_2), the wavelength of maximum absorption is bathochromically shifted by 22, 28 and 25 for Dye 1, Dye 2 and Dye 3, respectively as compared to the corresponding spectra in solution, implying that dyes adsorbed on to the TiO_2 surface contain partial J-type aggregates [26-28].

The molar extinction coefficients of Dye 1 and Dye 2 in THF at their respective λ_{max} are also shown in Table 1, indicating that these novel dyes have good light harvesting abilities [29]. The fluorescent characteristics of dyes measured in DMF are represented in Table 1. In DMF solution, dyes show intense green fluorescence due to the charge transfer from the electron donating group to the accepting group. The fluorescence emission maxima of the synthesized Dye 1, Dye 2 and Dye 3 in the DMF are 628, 644 and 632, respectively.

Table 1: Absorption properties of the synthesized dyes.

Dye	λ_{max}(nm)[a]	ε ($M^{-1}cm^{-1}$)	λ_{max}(nm)[b]	λ_F(nm)[a]
1	530	29742	552	628
2	558	28813	591	644
3	550	28654	575	632

a) DMF:H_2O = 1:1, b) on photoanode (TiO_2) substrate

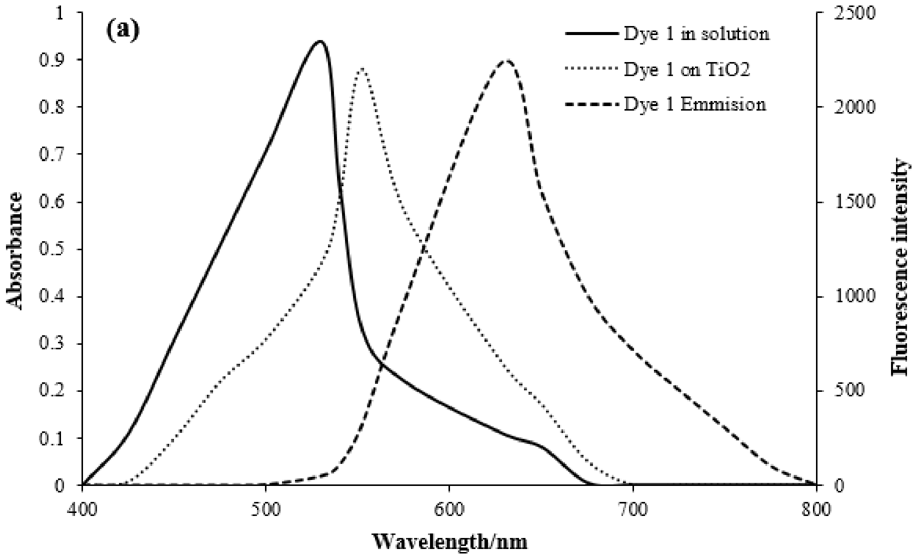
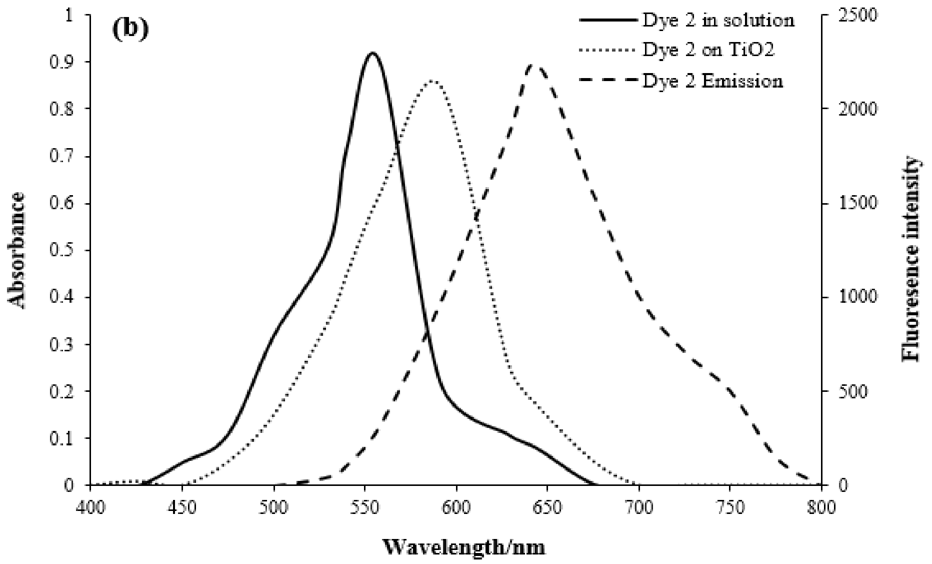


Figure 2: UV-Vis absorption and fluorescence spectra of a) Dye 1, b) Dye 2 and c) Dye 3.



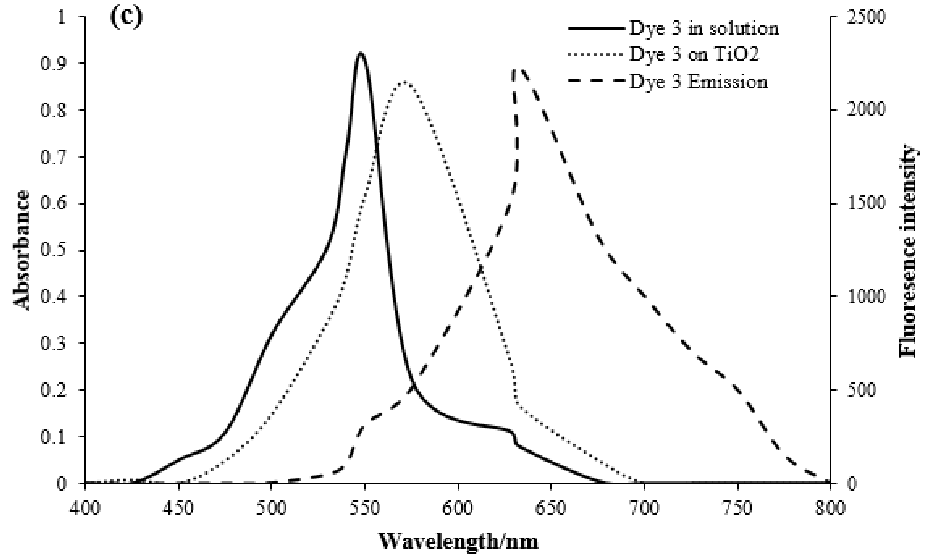


Figure 2: Continued.

The oxidation potential (E_{ox}) of Dye 1, Dye 2 and Dye 3 was measured in acetonitrile by cyclic voltammetry. There are two distinct redox waves observed in the voltammogram. The first oxidative wave (I) was due to the oxidation of the internal standard of ferrocene, whereas the second wave (II) near was due to the electrochemical oxidation of Dyes. The oxidation peak potential (Epa) for Dye 1, Dye 2 and Dye 3 can therefore be calculated to be +1. 22 V, +1.16 V and +1.19 vs F_c/F_c^+ in acetonitrile, respectively. Although the standard E_{ox} value is usually not easily obtained experimentally, it can be approximately estimated from the cyclic voltammetric peak potential method, which equals it if the electrochemical oxidation is a reversible step [30]. The E_{ox}-E_{0-0} level of Dye 1, Dye 2 and Dye 3 is calculated to be –0.77 V, –0.79 V and –0.82 V vs F_c/F_c^+ in acetonitrile.

Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behavior of Dye 1, Dye 2 and Dye 3 dye molecules and their structures. The DSSCs utilized these dyes as sensitizers for nanocrystalline anatase TiO_2. A typical photocurrent–photovoltage (J–V) curve for cells based on Dye 1, Dye 2 and Dye 3 is depicted in Figure 3. The detailed photovoltaic parameters are also summarized in Table 2. The solar energy to electricity conversion efficiency (η) of the DSSCs is calculated from short circuit current (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (P_{in}) [30, 31].

According to the results shown in Table 2, under the standard global AM 1.5 solar condition, the conversion efficiencies of cells containing Dye 1, Dye 2 and Dye 3 are 2.11%, 2.32%and 2.17%, respectively. The larger conversion efficiency of Dye 2 sensitizer is probably due to the stronger electron withdrawal ability of the combination of two sulfonic acid groups. The conversion efficiency of solar energy to electricity of the present organic dyes could be improved by extending the conjugated length of the organic dyes or by incorporation of a thiophene π-bridge [26, 32-35].

Table 2: Photovoltaic performance of DSSCs based on Dye 1 and Dye 2.

Dye	V_{OC} (V)	J_{SC} ($mA.cm^{-2}$)	FF	η (%)
1	0.65	4.92	0.66	2.11
2	0.65	5.41	0.66	2.32
3	0.65	5.06	0.66	2.17

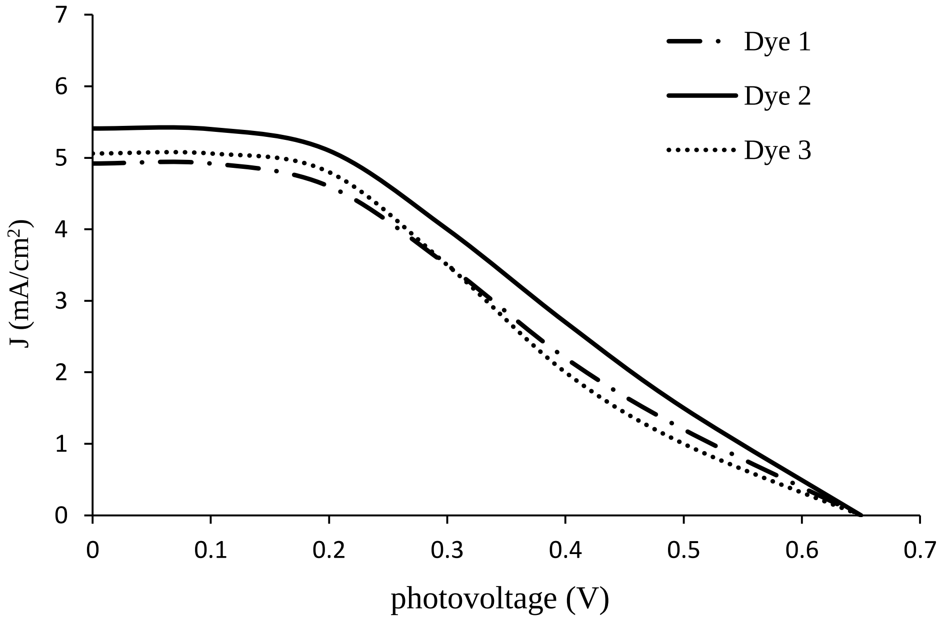


Figure 3: Current density-voltage characteristics for Dye 1, Dye 2 and Dye 3.

4. Conclusions

It may be summed up from this review that cotton is one of the prominent fibers used mostly. The reactive dye is mostly used for the dyeing of cotton, which can be bonded with cotton fabric by two mechanisms mentioned above. The cotton can be dyed by both exhaust and continuous methods. The main problem of cotton dyeing industry is the water pollution obtained in the result of dyeing of cotton. Recently, various strategies have been made to overcome this problem. These strategies include changes in the dye structure, changes in dyeing machinery, chemical modification of cotton fabric and use of eco-friendly auxiliaries in the dyeing of cotton.

Conflict of interest

The authors declare that there is no conflict of interest.

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