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Investigation of effect of anti-aggregation agent on the performance of nanostructure dye-sensitized solar cells

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Dye sensitized solar cells (DSSCs) based on indigo dyes exhibit suitable conversion efficiency. These organic dyes have been undergone for aggregation. Electron transfer process is reduced due to an aggregation of molecular dyes. Therefore, anti-aggregation agent is commonly utilized in fabrication of DSSCs. In the present study, two anti-aggregation agents namely as 3α,7α-dihydroxy-5β-cholanic acid (cheno) and 3α,7α,12α-trihydroxy-5β-cholanic acid (cholic acid) were added to indigo dye solution in DSSCs in order to determine the photovoltaic parameters such as short circuit photocurrent, open circuit voltage and conversion efficiency of each individual dye in the absence and presence of anti-aggregation agents. The results show that the conversion efficiencies are improved with reduced aggregation. Spectrophotometric evaluations of the indigo dyes in solution and on a TiO_2 substrate were carried out in the absence and presence of anti-aggregation agents in order to estimate changes in the status of the dyes in different environments. J-type aggregates on the nano TiO_2 are reduced in the presence of anti-aggregation agents.

Keywords: dye sensitized solar cells, sensitizers, indigo dyes, anti-aggregation agent, photocurrent-photovoltage curves, conversion efficiencies.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been investigated extensively as a topic of research in the field of renewable energy resources [1]. Inorganic dye molecules are commonly utilized in DSSCs but, metal free organic dyes that are environmentally friendly and easily synthesized have been utilized in DSSCs in 1993 [2,3]. Several types of dyes such as coumarin dyes, polyene dyes, hemicyanine dyes, thiophene based dyes and indoline dyes have been prepared for a DSSCs' application [4,5]. The highest overall power conversion efficiency (PCE) values that have been reported for DSSCs sensitized with polypridyl ruthenium dyes are 11%, with porphyrin dyes 12.3%, and with metal-free organic dyes ~10% [6]. However, the limitations of metal-free organic dyes are reduced in a conversion efficiency due to dye aggregation because dye aggregation inhibits electron transfer from the exited dye to a TiO_2 substrate [1]. Therefore, anti-aggregation agents are commonly utilized in a dye solution to improve the electron transport resulting in greater DSSCs' performance [7]. Ito *et al*. investigated the effect of adding anti-aggregation agent to indole an organic dye in DSSCs' performance [8]. The results showed that addition of anti-aggregation to a dye solution improved DSSCs' performance [2,9].

However, exact contribution of anti-aggregation in DSSCs' performance based on indigo dye is not clearly reported. In this study, we disclose the high efficiency DSSCs with the use of anti-aggregation agent. The spectrophotometric properties of the indigo dye in solution and on a nano anatase TiO_2 substrate were also examined. The structures of dye molecules and anti-aggregation agents are given in Fig. 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 and organic dyes (Dye 1 and Dye 2) have been described in the literature [10]. UV-Visible spectrophotometry was carried out on a Dupont 2000 DSC instrument and a Cecil 9200 double beam transmission spectrophotometer. The fluorescence spectra of dye solutions were obtained by Osean Optics Usb2000flg Fluo-

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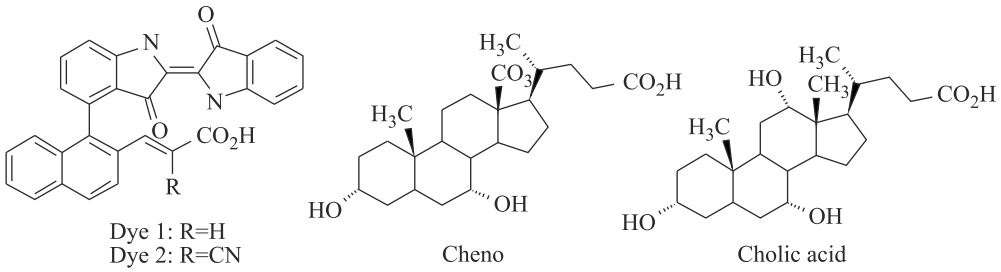

Fig. 1. Structures of dye molecules and anti-aggregation agents.

rometer. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra, using fluorescein as standard (Φ_{ref} = 0.95).

2.2. Dye-sensitized solar cells assembly and photovoltaic characteristics of the resultant solar cells

A nanocrystalline anatase TiO_2 past was coated on a transparent glass support. Each individual dye was adsorbed by dipping a separate coated glass in a 5×10^{-5} M ethanolic solution of each dye in the absence and presence of anti-aggregation agent such as 3α,7α-dihydroxy-5β-cholanic acid (cheno) and 3α,7α,12α-trihydroxy-5β-cholanic acid (cholic acid) for several hours. The visible bands in the absorption spectrum of the dyes after adsorption on a nano TiO_2 film only appeared after the TiO_2 electrodes were dipped in the dye solution for at least 18 hours. Finally, the film was washed with a 1:1 acetonitrile:ethanol mixed solution. Acenonitrile:ethylenecarbonate (v_A/v_e = 1:4) containing tetrabutyl ammonium iodide (0.5 mol dm^{-3}) was used as an electrolyte. Each dye-adsorbed TiO_2 electrode, together with a Pt counter electrode and the mentioned electrolyte solution were separately assembled into a sealed sandwich type solar cell [11–14]. For each solar cell 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 $mWcm^{-2}$) through a shading mast (5.0 mm×4 mm) by using a Bunko-Keiki CEP-2000 system.

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} [15].

3. Results and discussion

The structures of the considered organic dye molecules and anti-aggregation agents have been presented in Fig. 1. The wavelength of maximum absorption (λ_{max}) for the synthesized dyes in THF are presented in Table 1 and UV-Vis spectra of Dye 1 is illustrated in Fig. 2, together with λ_{max} of the corresponding dyes adsorbed on a TiO_2 film in the absence and presence of anti-aggregation agents. Under similar conditions, D2 shows a bathochromic shift in the absorption peak to 572.5 nm which can be attributed to the presence of an electron acceptor group (-CN) that was linked to the vinyl bridge. This bathochromic shift arises from the fact that one more electron acceptor (-CN) increases electron withdrawing ability of the electron acceptors' group and lowers the lower unoccupied molecular orbital, thus, reducing the gap between higher and lower unoccupied molecular orbital states [16]. The molar extinction coefficients of Dye 1 and Dye 2 in THF are also 37383 and 37429 $LM^{-1}cm^{-1}$, respectively, indicating that these dyes have good light harvesting abilities. Upon a dye adsorption onto a TiO_2 surface, the λ_{max} is bathochromically shifted by 19.5 and 22.5 nm for Dye 1 and Dye 2, respectively as compared to the corresponding spectra in solution, implying that dyes adsorbed onto a TiO_2 surface contain partial J type aggregates. The λ_{max} for the dye adsorption onto a TiO_2 surface is bathochromically shifted by 7.5 nm and 9 nm for Dye 1 and Dye 2 in the presence of cheno and 11.5 nm and

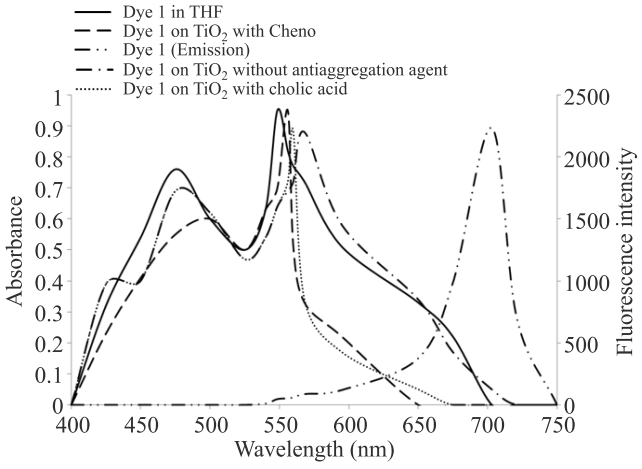

Fig. 2. UV-Vis absorption and fluorescence spectra for dyes Dye 1.

12.5 nm in the presence of cholic acid, respectively. The results show that bathochromic shifts in the wavelength of maximum absorption reduced due to presence of the anti--aggregation agents and cheno as anti-aggregation agent have better performance compared to the cholic acid.

Table 1. The wavelength of maximum absorption of synthesized dyes.

Dye	λ_{max} (nm) in THF [10]	λ_{max} (nm) on TiO_2 in the absence of anti--aggregation agent	λ_{max} (nm) on TiO_2 in the presence of cheno	λ_{max} (nm) on TiO_2 in the presence of cholic acid
Dye 1	548.5	568	556	560
Dye 2	572	595	581.5	585

The fluorescent properties of the synthesized dyes in THF are also listed in Table 2. In THF solution, dyes depict intense green fluorescence due to the charge transfer from the electron-donating entity to the electron-accepting entity. The λ_F of the indigo dyes in the THF are 703 nm and 721 nm for Dye 1 and Dye 2, respectively.

Table 2. Emission properties of synthesized dyes.

Dye	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	E_F	Φ_F
Dye 1	703	4144	0.28	0.38
Dye 2	721	4158	0.25	0.33

The oxidation potential (E_{ox}) of Dye 1 and Dye 2 was measured in acetonitrile by cyclic voltammetry [17]. The oxidation peak potential (E_{ox}) for Dye 1 and Dye 2 can, therefore, be calculated to be 0.57 and 0.52 vs Fc/Fc^+ in acetonitrile, respectively (Fig. 3). The E_{red} of Dye 1 and Dye 2 is estimated to be –1.31 and –1.33 V vs Fc/Fc^+ in acetonitrile. Therefore, the synthesized dyes are suitable for use in dye sensitized solar cells. The excited state oxidation potentials (LUMO) of Dye 1 (–1.31 V) and Dye 2 (–1.33 V) are both more negative than the conduction band gap edge of TiO_2 [–0.5 V (*vs*. NHE)]. Provided that an energy gap (between the dye LUMO state and the conduction band of TiO_2) of 0.2 eV is necessary for efficient electron injection [18], the driving force is sufficient for efficient charge injection. Thus, the electron injection process from each excited dye molecule to the TiO_2 conduction band and the subsequent dye regeneration are energetically permissible. The energy levels of the ground state (HOMO) of D1 (0.57 V) and D2 (0.52 V) are sufficiently more positive than the I_3^-/I^- redox potential [(0.42 V (*vs*. NHE)] [11,12,19], indicating that the oxidized dye formed after electron injection into the conduction band of TiO_2 could accept electrons from I^- ions in the electrolyte, being thermodynamically favourable. Such electronic structures thus ensure a favourable exothermic flow of charge throughout the photo-electric conversion.

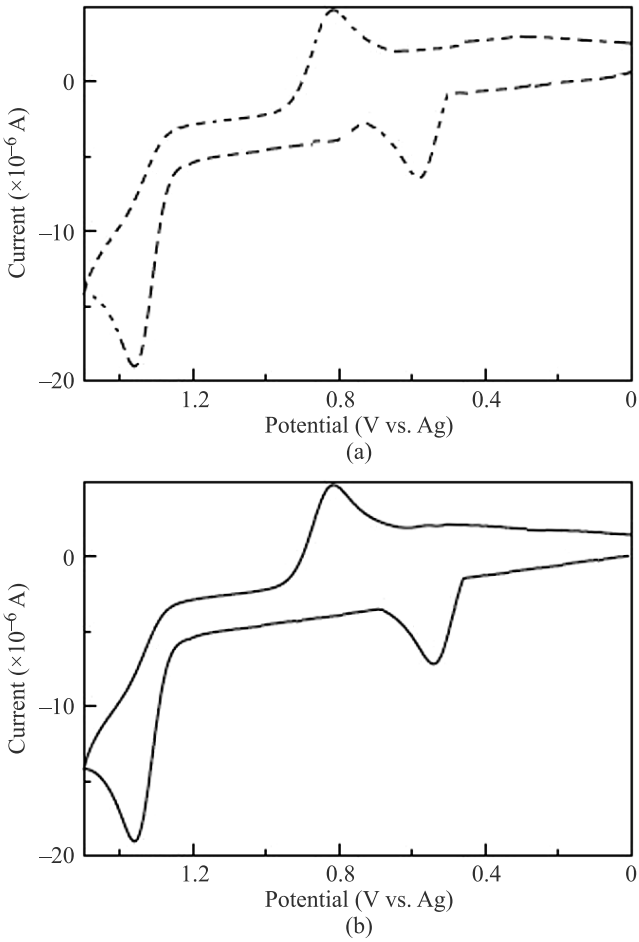

Fig. 3. Cyclic voltammetric curve for (a) Dye 1 and (b) Dye 2.

The photovoltaic properties of each dye was attained and compared to clarify the relationship between sensitizing behaviours of Dye 1 and Dye 2 and their effect of anti--aggregation agents. Detailed photovoltaic parameters of Dye 1 and Dye 2 in the absence and presence of the anti--aggregation agents are also summarized in Table 3. The solar energy to electricity conversion efficiency (η) of the

Table 3. Photovoltaic performance of DSSCs based on D1 and D2.

Photovoltaic properties	In the absence of anti-aggregation agent [10]		In the presence of cheno		In the presence of cholic acid	
	Dye 1	Dye 2	Dye 1	Dye 2	Dye 1	Dye 2
J_{SC} ($mA \cdot cm^{-2}$)	7.47	8.55	8.75	10.79	8.51	9.79
V_{OC} (V)	0.64	0.63	0.64	0.63	0.64	0.64
FF	0.65	0.64	0.66	0.65	0.67	0.67
η (%)	3.11	3.45	3.7	4.42	3.65	4.2

DSSCs is calculated from the short circuit current (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (Pin) according to Eq. (1) [20]. Photocurrent–photovoltage (J–V) curves of cells based on Dye 1 are illustrated in Fig. 4.

$$\eta = \frac{J_{SC}(mA \cdot cm^{-2})[V_{OC}(V)][FF]}{P_{in}(mV \cdot cm^{-2})} \quad (1)$$

The results carried out under the standard global AM 1.5 solar condition and shown in Table 2 demonstrate that the maximum value of the conversion efficiency of solar cells containing Dye 2 was achieved. The larger conversion efficiency of Dye 2 sensitizer is probably due to the stronger electron acceptor ability of the cyanoacrylic acid. The conversion efficiency of solar energy to electricity of such organic dyes could be improved by using completely different substituted [21,22] or by addition anti-aggregation agent. Reduced aggregations of dye are directly correlated with faster electron transfer from excited state of dye to TiO_2 substrate in solar cell. Therefore, designing highly flexible and conjugated organic dye molecules are essential for absolute harvesting of sun light in dye sensitized solar cells. Thus, conversion efficiency of dye sensitized solar cells is directly correlated with larger conformational flexibility and diffusion values of organic dye molecules [1].

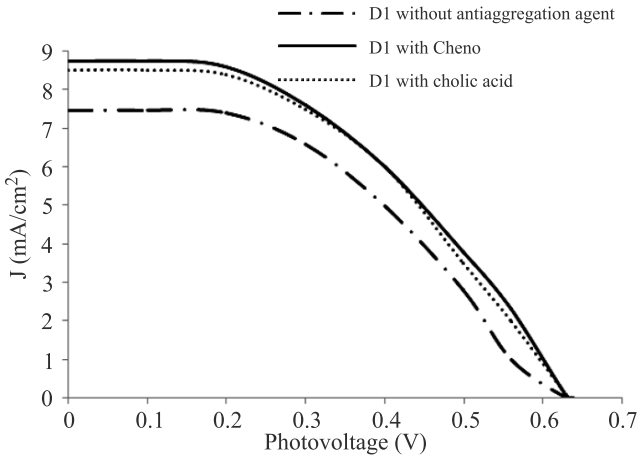

Fig. 4. Current density-voltage characteristics for D1 in the absence and presence of anti-aggregation agents.

4. Conclusions

Metal-free organic dyes of a type (D-π-A) based on indigo as potential sensitizers for DSSCs exhibit suitable conversion efficiency. Two new metal-free organic dyes based on indigo were synthesized and the spectrophotometric properties of the prepared organic dyes in THF solvent and on TiO_2 films in the absence and presence of anti-aggregation agents were examined. In all cases, the absorption maxima of Dye 1 and Dye 2 applied on the surface of a nano anatase TiO_2 film gave bathochromic shifts compared to the corresponding dye spectra in THF solution. The results show the dyes from J-type aggregates on the TiO_2 substrate but, the amounts of aggregation were reduced in the presence of anti-aggregation agents. Electron transfer process is reduced due to aggregation of molecular dyes. So, anti-aggregation agent is utilized in fabrication of DSSCs. The results show that the conversion efficiencies are improved with reduced aggregation. For example D1 indicated 3.11%, 3.7% and 3.65% for conversion efficiency in the absence of anti--aggregation agent, in the presence of cheno and in the presence of cholic acid, respectively. Thus, conversion efficiency of dye sensitized solar cells is directly correlated with larger conformational flexibility and diffusion values of organic dye molecules.

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