



Investigation of Indigo/thioindigo Tandem Dye-Sensitized Solar Cells

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ABSTRACT

In this paper we used two free-metal organic dyes (dye 1 and dye 2) based on indigo and thioindigo with cyanoacrylic acid as the electron acceptor group. The proposed dyes were sensitized from naphalene as the starting material by standard reactions and characterized by different analytical techniques and UV-Visible spectroscopy after purification. Spectrophotometric measurements of the organic dyes in solution and on a TiO₂ substrate were carried out in order to assess changes in the status of the dyes. The wavelengths of maximum absorption for dye 1 and dye 2 in solution were 572 nm and 492.3 nm and on TiO₂ films were 595 nm and 516.8 nm, respectively. Finally, the proposed dyes were used as sensitizer in DSSCs and T-DSSCs structure and their photovoltaic properties were investigated. The Conversion efficiency for dye 1 and dye 2 in DSSCs and T-DSSCs were 3.45% and 6.45% and 4.09%, respectively. Prog. Color Colorants Coat. 10 (2017), 239-244 © Institute for Color Science and Technology.

1. Introduction

Dye-sensitized solar cells (Gratzel cells or DSSCs) are the most attractive among all photovoltaic devices due to low cost of fabrication and eco-friendly properties [1-3]. Mathew et al. have prepared dye-sensitized solar cell with efficiency of 13% [4] and Liska et al. have reported an efficiency of 15% for nanocrystalline dye-sensitized solar cell/copper indium selenide thin film [5], however, they suggested that further improvements are needed in DSSCs efficiency. Increased light harvesting from the visible to the near infrared region has been reported using a panchromatic sensitizer [6]. Mixing different sensitizers that absorb light in different regions of the solar spectrum seems to be a promising approach, but the power conversion

efficiency is not much enhanced [7-9]. Another method of increasing the region of absorption is to use a tandem structures, where two single cells are connected in series [10, 11]. In tandem dye-sensitized solar cells (T-DSSCs) structure, the top cell use a shorter wavelength region of the incoming light and the bottom cell harvests light from longer wavelength [12]. By matching the photocurrent density of the top and bottom cells, the sum of the open-circuit voltage ($V_{oc, top} + V_{oc, bottom}$) of the top and bottom cells is achieved [13]. In T-DSSCs, light reaching the bottom electrode has to pass through at least three transparent conductive oxide layer, during which losses in photon harvesting occur [12, 14]. A hybrid cell consisting of a top electrode (FTO glass/TiO₂ layer stained with

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N3)/electrolyte/Pt mesh electrode/electrolyte/a bottom electrode (TiO₂ stained with black dye)/FTO glass has been reported. The Pt electrode is inserted in an electrolyte layer between the top electrode and the bottom electrode. These two titania electrodes were connected in parallel [15]. A tandem cell consisting of a top electrode (FTO glass/TiO₂ stained by N3) and a bottom electrode (NiO stained by Erythrosin B/FTO glass) has been reported [16, 17].

In the present study two metal-free organic dyes based on indigo and thioindigo were used as the sensitizer. The dyes together with their corresponding intermediates were then purified and characterized. The spectrophotometric properties of the organic dyes in THF solvent and on the nano-anatase TiO₂ substrate were examined. The absorption maxima and the intensities of the resultant dyes were also obtained. Dye sensitized solar cells and tandem-sensitized were then fabricated utilizing these metal-free organic dyes and their photovoltaic behaviors were determined.

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 organic dyes (dye 1 and dye 2) are described elsewhere [18, 19]. Transparent conducting oxide, FTO (F-doped SnO₂, DyeSol), TiO₂ pastes, scattering layer (Sharif Solar Co.) and Di-tetrabutylammoniumbis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719, Sharif Solar Co.) were purchased. UV-visible spectrophotometry was carried out on a Cecil 9200 double beam transmission spectrophotometer to obtain molar extinction coefficients and absorption maxima.

2.2. Fabrication of tandem dye-sensitized solar cells and characterization

T-DSSCs consisting of four plates (conventional mechanical tandem) were prepared in the following device configuration: FTO glass/TiO₂/dye A/electrolyte/semi-transparent Pt-FTO glass/FTO glass/TiO₂/dye B/electrolyte/Pt-FTO glass. The FTO glasses were cleaned sequentially with distilled water, acetone, isopropyl alcohol and distilled water and were subjected to UV-ozone treatment to remove organic impurities and make a hydrophilic surface. A nanocrystalline TiO₂ film was coated on a transparent glass support. The sample

was immersed in a 0.3 mM solution of indigo dye in $\times 10^{-5}$ M ethanolic solution of the dye containing 7% 4-tert-butylpyridine and 50 mM 3 α ,7 α -dihydroxy-5 β -cholic acid (cheno) for 48 h at room temperature. The sample was immersed in a 0.5 mM solution of thioindigo dye in $\times 10^{-5}$ M ethanolic solution of the dye containing 7% 4-tert-butylpyridine and 50 mM 3 α ,7 α -dihydroxy-5 β -cholic acid (cheno) for 4 h at room temperature. For the counter electrode in the top cell, a semi-transparent catalytic Pt layer was deposited on an FTO glass via sputtering. The T-DSSC was then fabricated by mechanically stacking the top cell bearing the thioindigo-sensitized photo anode on the bottom cell. The electrolyte used in both cells consisted of I₂ (50 mM), LiI (500 mM), 4-tert-butyl pyridine (580 mM) and 1-ethyl-3-methylimidazolium iodide (600 mM) in dehydrated acetonitrile [12].

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 mask (5.0 mm \times 4 mm) by using a Bunko-Keiki CEP-2000 system.

3. Results and Discussion

The organic dyes 1 and 2 were synthesized in a similar way as described in the literature [18, 19]. The 1-bromo-2-yl-naphthalene was reacted with cyanoacrylic acid by the Knoevenagel reaction in the presence of piperidine, and then the residue was reacted by 4-bromoindoxyl or 4-bromothioindoxyl, respectively. The second key reaction step in synthesizing was accomplished using the Ullmann coupling reaction. This type of coupling procedure was first reported in 1901 by Ullmann as a reaction that generates a carbon-carbon bond between two aromatic nuclei [20], so the naphthyl substituent is located in the 4-position. The procedure involves heating a mixture of aryl halides with copper powder or copper bronze at 100-360 °C either with or without a solvent. Finally, dye 1 and dye 2 were synthesized through the respective reaction of residues with LiOH. The chemical structures of organic dyes are depicted in Figure 1.

The wavelength of maximum absorption (λ_{\max}) and the molar extinction coefficients (ϵ_{\max}) for the synthesized dyes in THF are listed in Table 1 and shown in Figure 2, together with the λ_{\max} of the corresponding dyes adsorbed on the TiO₂ film. The absorption peaks for the synthesized dyes can be

assigned to an intra-molecular charge transfer between the donor and the acceptor groups [21], providing an efficient charge-separation for the excited state. The wavelength of maximum absorption was around 485 nm for dye 2. 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 organic dyes

have good light harvesting abilities [22]. Upon dye adsorption on to a photo-anode surface, the wavelength of maximum absorption is bathochromically shifted by 23 and 24.5 nm for dye 1 and dye 2, respectively, as compared to the corresponding spectra in the solution, implying that dyes adsorbed on to the TiO_2 surface contain partial J-type aggregates [23-25].

Table 1: Absorption properties of the organic dyes.

dye	$\lambda_{\max}(\text{nm})^a$	$\epsilon (\text{M}^{-1}\text{cm}^{-1})$	$\lambda_{\max}(\text{nm})^b$	$\lambda_f(\text{nm})^a$
1	572	37429	595	721
2	492.3	36429	516.8	595

a) Acetonitrile solution, b) on photoanode substrate.

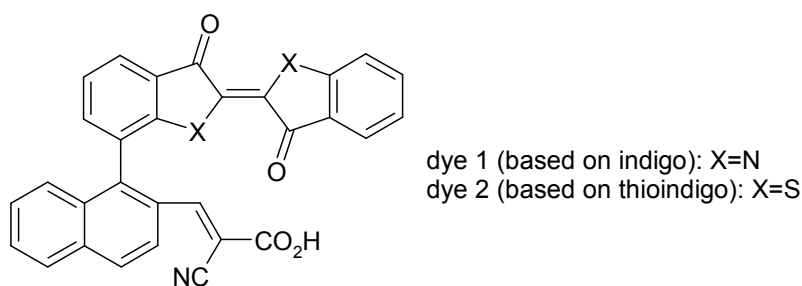


Figure 1: Chemical structures of used organic dyes.

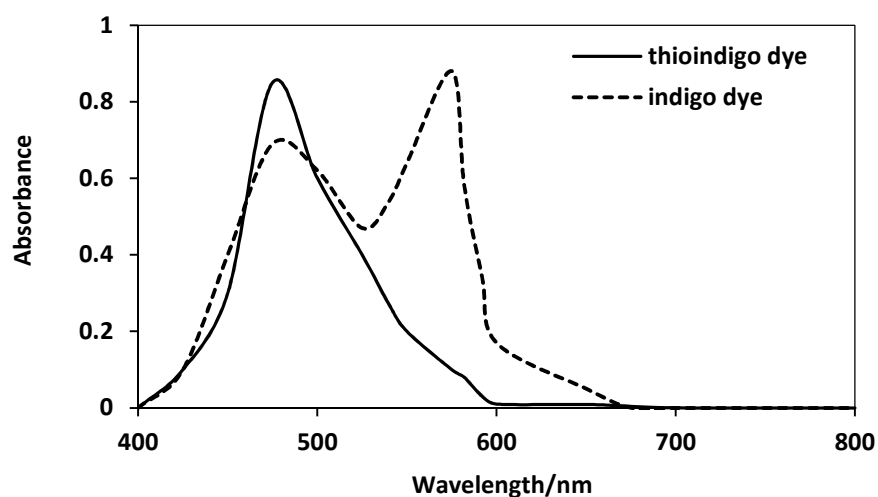


Figure 2: UV-Vis absorption spectra of organic dyes.

Dye-sensitized solar cells (DSSCs) and T-DSSCs were constructed and compared in order to clarify the relationships between the sensitizing behavior of dye 1 and dye 2 dye molecules and their structures. The DSSCs utilized synthesized organic dyes as sensitizers for nanocrystalline anatase TiO_2 . A typical photocurrent–photovoltage (J – V) curve for DSSCs and T-DSSCs based on organic dyes 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}) [26, 27]. A tandem cell consisting of a top cell (FTO glass/ TiO_2 stained by an indigo dye/electrolyte layer/FTO glasses) and a bottom cell (FTO glass/ TiO_2 stained by a thioindigo dye/electrolyte layer/FTO glasses) has been prepared. The working principle of tandem cell (T-DSSCs) has

been shown in Figure 3. The thioindigo dye in the top electrode is excited and electrons are excited from the highest occupied molecular orbital (HOMO) top electrode to the lowest unoccupied molecular orbital (LUMO) top electrode, followed by injection from the dye into the porous TiO_2 layer and collection by the FTO layer on the front of the cell. The light passing through the top electrode and the FTO layer in the middle reaches the bottom electrode, which is stained with the indigo dye [28–30]. The complementary electronic absorption spectra of dyes indigo and thioindigo (Figure 2) indicates that the photons with long wavelengths, which were not absorbed by the top cell, are now available for the bottom cell. The electrons of the indigo dye in the bottom electrode are excited from the (HOMO) bottom cell to the (LUMO) bottom cell [12, 31]. The electrons at the counter electrodes reduce the I_3^- in electrolytes to I^- , which leads to the regeneration of the dye [32].

Table 2: Photovoltaic performance of DSSCs.

structure	V_{oc} (V)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	FF	η (%)	Ref.
dye 1	0.63	8.55	0.64	3.45	18
dye 2	0.73	12.99	0.68	6.45	19
tandem	0.84	6.78	0.71	4.09	This work

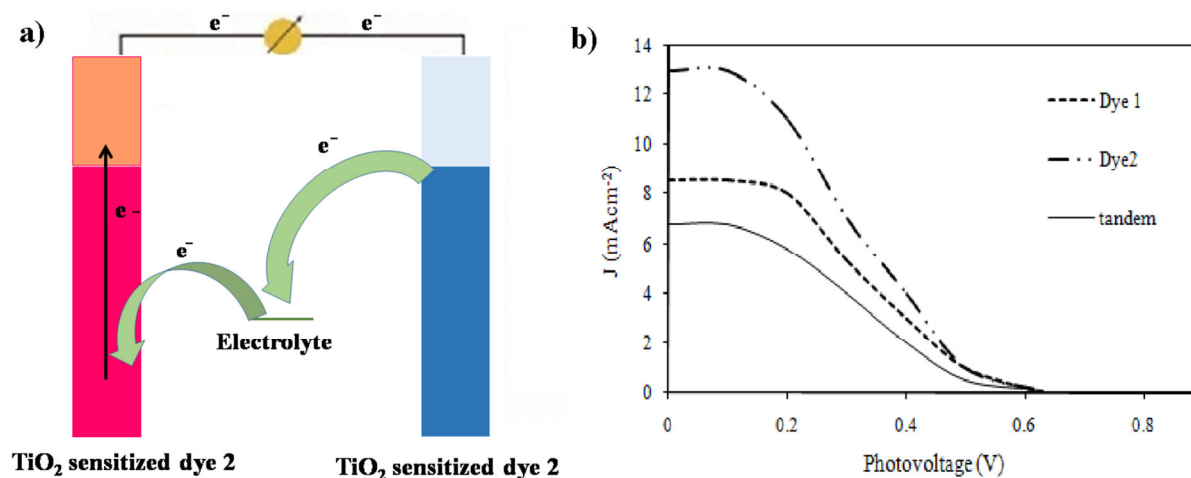


Figure 3: a) Working principle of tandem cell and b) Current density-voltage DSSCs.

4. Conclusions

Two metal-free organic dyes (D- π -A) as sensitizers in DSSCs were designed and synthesized based on indigo and thioindigo by employing cyanoacrylic acid as acceptor units. The synthesized dyes were identified by FT-IR, ¹HNMR, ¹³CNMR, elemental analysis and UV-Visible spectroscopic techniques. The spectrophotometric properties of the prepared organic dyes in solvent and on TiO₂ films were examined. The absorption maxima of dye 1 and dye 2 and applied on the surface of a TiO₂ film gave a bathochromic effect compared to the corresponding dye spectra in solution. Finally, the photovoltaic behavior of the prepared dyes was assessed after utilizing them in constructed DSSCs

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