

Application of Azo Dye as Sensitizer in Dye-Sensitized Solar Cells

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ARTICLE INFO

Article history:

Received: 08-08-2015

Final Revised: 25-08-2015

Accepted: 02-09-2015

Available online: 02-09-2015

Keywords:

Dye-sensitized solar cells

Sensitizers

Photovoltaic materials

Conversion efficiencies

Azo dye

ABSTRACT

An azo dye is used as photosensitizers in Dye-sensitized solar cells. Azo dyes are economically superior to organometallic dyes because they are color variation and cheap. The spectrophotometric evaluation of an azo dye in solution and on a TiO₂ substrate shows that the dye forms J-aggregation on the nanostructured TiO₂ substrate. Oxidation potential measurements for used azo dyes ensured an energetically permissible and thermodynamically favorable charge transfer throughout the continuous cycle of photo-electric conversion. The performance of dye-sensitized solar cells based on azo dyes has been studied. The results illustrate that the dye containing acetic acid and sulfonic acid as the acceptor group gave the maximum conversion efficiency of 3.52% and 3.17% in the presence and absence of anti-aggregation agent, respectively. Prog. Color Colorants Coat. 8 (2015), 259-265 © Institute for Color Science and Technology.

1. Introduction

Dye-sensitized solar cells (Grätzel cells or DSSCs) have attracted much attention as potential resource energy due to their efficient conversion of solar energy to electricity at low cost [1]. In recent years, different photosensitizers have been designed and applied to DSSCs [2]. Organometallic dyes indicated overall conversion efficiency over 12% [3]. But their application is limited due to high cost and complex method [1]. Many organic dyes inclusive of coumarine [4], polyene [5], hemicyanine [6], thiophene based [7], and indoline [8] dyes exhibiting relatively high

performances in dye-sensitized solar cells have so far been designed and developed. In such compounds the electron-donating and electron-accepting groups are connected through a π -conjugated linker (a D- π -A molecular structure). Their properties can be finely tuned by independently altering, alternating or matching different groups in such D- π -A dyes. In research for high efficiency organic dyes for solar cells, development of new materials offering optimized thermal and photochemical stabilities, as well as appropriate optical and electrical properties is of

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utmost importance [9]. Azo dyes combine their optical and electronic properties with good chemical stability and solution process ability which can be used in Dye-sensitized solar cells (DSSCs). [1]. There is few reports about application of azo dyes as photosensitizers on DSSCs. Mikroyannidis et al. investigated the application of three new azo dyes in DSSCs. The results show that the overall power conversion efficiency (PCE) of the DSSCs is 2.59-4.17% for synthesized organic azo dye [10].

In this study, we have selected an azo dye with different substituents for the first time and investigated the performance of DSSCs in the absence and presence of the anti-aggregation agent. The spectrophotometric properties of organic dye in solution and on TiO₂ substrate and the electrochemical measurements are also investigated. Finally, we fabricated DSSCs using azo dye as photosensitizers and presented photovoltaic properties. The structures of the azo dye molecule are 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 food azo dyes were obtained from Institute of Standard and Industrial Research of Iran. Photo electrodes were fabricated using TiO₂ paste from Sharif solar. UV-visible spectrophotometry and fluorimetry were carried out on a Cecil 9200 double beam transmission spectrophotometer and Ocean Optics Usb2000flg fluorometer, respectively.

2.2. Electrochemical measurements

Electrochemical measurements of the food azo dye was 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 counter electrodes. All electrode potentials were calibrated with respect to ferrocene(Fc)/ferrocenium (Fc^+) redox couple. 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} [11].

2.3. Dye-sensitized solar cell assembly and photovoltaic characteristics of the resultant solar cell

A nanocrystalline anatase TiO₂ film was coated on a transparent glass support. The individual food azo dye was adsorbed by dipping a separate coated glass in a $5 \times 10^{-5} \text{ M}$ solution of dye containing for 12 hours. The visible bands in the absorption spectrum of the dye after adsorption on nano TiO₂ film only appeared after the TiO₂ electrodes were dipped in the dye solution for at least 12 hours. Finally, the film was washed with a 1:1 acetonitrile:ethanol mixed solution. Acetonitrile-ethylenecarbonate (v/v=1:4) containing tetrabutyl ammonium iodide (0.5 mol dm^{-3}) was used as an electrolyte. The dye-adsorbed TiO₂ electrode, together with a Pt counter electrode and the mentioned electrolyte solution were separately assembled into a sealed sandwich type solar cell [12]. For solar cell, an action spectrum was measured under monochromatic light with a constant photon number ($5 \times 10^{15} \text{ photon cm}^{-2} \text{ s}^{-1}$). Photocurrent-photovoltage (J-V) characteristic was 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..

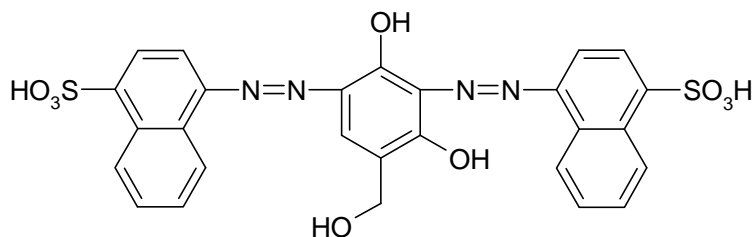


Figure 1: Chemical Structure of azo dye.

3. Results and discussion

A disazo acid dye with general structure shown in Figure 1 containing sulfonic acid was chosen. The acid azo dyes had brown hue. Azo dyes containing one azo group (monoazo), two azo groups (disazo), three azo groups (trisazo) or more don't exist naturally. Azo dyes are accounted for approximately 60-70% of all synthesized dyes utilized in industry. Azo dyes have applications such as reversible optical storage media, chiroptical switches, electrooptic modulators and chemical sensors [10]. Recently, more attention has been directed to the application of azo dyes in photovoltaic devices because they are not only inexpensive but also they have relatively facile dye synthesis and chemical stability [10, 13].

The wavelength of maximum absorption (λ_{\max}) and the molar extinction coefficients (ϵ_{\max}) for the azo dye in Dimethylformamide (DMF) are listed in Table 1 and shown in Figure 2, together with the λ_{\max} of the corresponding dyes adsorbed on the TiO₂ film in the presence and absence of anti-aggregation agent. The absorption peaks at around 465 nm for azo dye can be

assigned to an intra-molecular charge transfer between the donor group and the acrylic acid group [14], providing an efficient charge-separation for the excited state. Upon dye adsorption on to a TiO₂ surface, the wavelength of maximum absorption is bathochromically shifted by 22.5 and 7 nm for azo dye in the presence and absence of anti-aggregation agent, respectively, as compared to the corresponding spectra in solution, implying that dyes adsorbed on to the TiO₂ surface contain partial J-type aggregates [15-17]. The molar extinction coefficients of azo dye in DMF at their respective λ_{\max} are also shown in Table 1, indicating that this novel dye has good light harvesting abilities [18].

The fluorescent characteristics of dye measured in DMF are represented in Table 1. In DMF solution, dye shows intense red fluorescence due to the charge transfer from the electron donating group to the accepting group. The fluorescence emission peak of the azo dye in the DMF is 572 nm.

Table 1: Absorption properties of synthesized dyes.

Dye	λ_{\max} (nm) ^a	λ_{\max} (nm) ^b	λ_{\max} (nm) ^c	λ_F (nm)
Azo dye	465	487.5	472	572

a) DMF solution, b) on TiO₂ substrate in the absence of anti-aggregation agent and c) on TiO₂ substrate in the presence of anti-aggregation agent

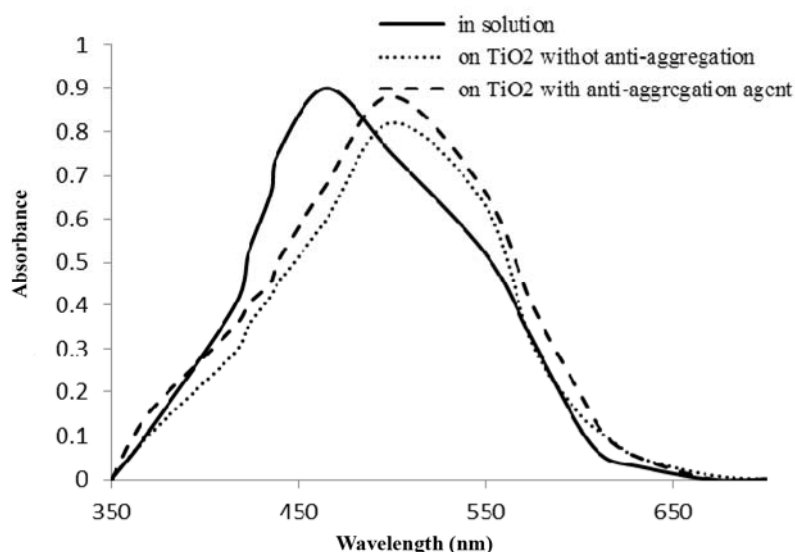


Figure 2: UV-Vis absorption of azo dye.

The oxidation potential (E_{ox}) of azo 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 attributed to the electrochemical oxidation of Dyes. The oxidation peak potential (E_{pa}) for azo dye can therefore be calculated to be +0.87 V vs Fc/Fc^+ in acetonitrile. Although the standard E_{ox} value is usually not easily obtained experimentally, it can be approximately estimated from the cyclic voltammetric peak potential, which equals it if the electrochemical oxidation is a reversible step [19]. No reduction peak was observed for the synthesized dyes. Therefore, the $E_{ox}-E_{0-0}$ level, where E_{0-0} represents the intersection of normalized absorption and the fluorescence spectra in DMF, was calculated. This is considered to correspond to the reduction potential [20]. The E_{0-0} of azo dye was observed at 630 nm corresponding to 1.87 eV. Therefore, the $E_{ox}-E_{0-0}$ level of azo dye is calculated to be -1.00 V vs Fc/Fc^+ in acetonitrile. A typical cyclic voltammetric curve for cells based on azo dye is depicted in Figure 3.

Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behavior of azo dye molecule and its structures. The DSSCs utilized this dye as photosensitizers for nanocrystalline anatase TiO_2 . A typical photocurrent–photovoltage ($J-V$) curve for cells based on azo dye is depicted in Figure 4. 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}) [21, 21].

Reduced aggregation of dye molecules directly related with faster electron transfer from the excited state of the dye molecules to the TiO_2 conduction band in DSSCs [11]. Therefore, anchoring highly dye molecules is critical for absolute adsorb of sunlight in DSSCs, thus, conversion efficiency directly depends to suitable dye deposition [11, 22]. Thus designing highly flexible and conjugated organic dye molecules are essential for absolute harvesting of sun light in dye sensitized solar cells [22].

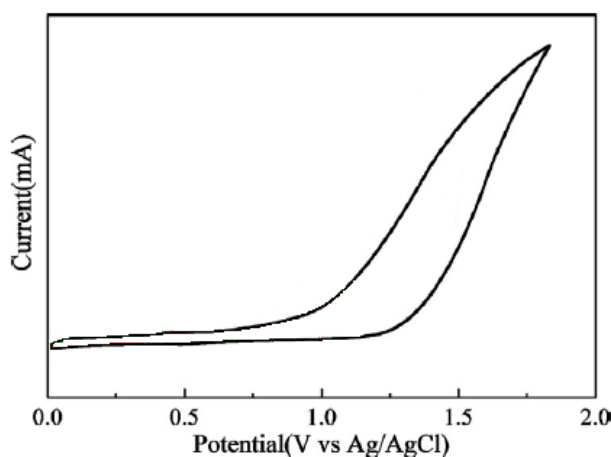
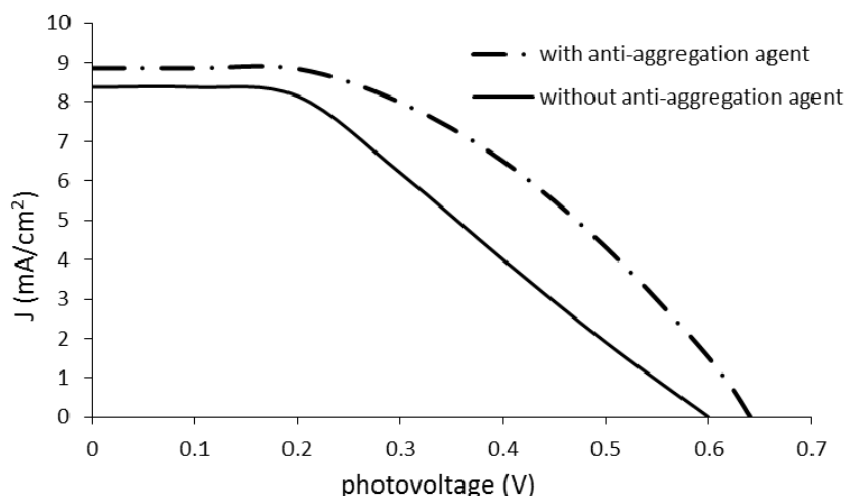


Figure 3: Cyclic voltammetric curve for azo dye.

Table 2: Photovoltaic performance of DSSCs based on azo dye

Photovoltaic properties	In the absence of anti-aggregation agent	In the presence of anti-aggregation agent
V_{oc} (V)	0.60	0.64
J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	8.38	8.87
FF	0.63	0.64
η (%)	3.17	3.52

**Figure 3:** Current density-voltage characteristics for azo dye.

4. Conclusions

A metal free organic dye as photosensitizer in DSSCs was selected based on azo dyes by utilizing a simple naphthyl residue as a part of π -conjugation system and a simple sulfonic acid as the electron acceptor anchoring group. The spectrophotometric properties of the azo dyes in solvent and on TiO_2 films in the absence and presence of the anti-aggregation agent were examined. According to the results, the absorption maxima of azo dyes separately applied on TiO_2 films gave bathochromic shifts compared to the corresponding dye spectra in the solutions. This is due to the form J-aggregate on the photoelectrode substrate,

but the amount of aggregation decreased in the presence of anti-aggregation agent because of the reduction in bathochromic shifts. Finally, the azo dye was utilized in DSSCs and its photovoltaic behavior was investigated. Solar energy to electricity conversion efficiencies of 3.17% and 3.52% were achieved for azo dye in the absence and presence of anti-aggregation agent, respectively.

Acknowledgement

The authors sincerely thank the Center of Excellence for Color Science and Technology for making this investigation possible.

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