



Highly efficient panchromatic dye-sensitized solar cells: Synergistic interaction of ruthenium sensitizer with novel co-sensitizers carrying different acceptor units



Dickson D. Babu ^a, Dalia Elsherbiny ^b, Hammad Cheema ^b, Ahmed El-Shafei ^{b, **},
Airody Vasudeva Adhikari ^{a, *}

^a Organic Materials Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India

^b Polymer and Color Chemistry Program, North Carolina State University, Raleigh, NC 27695, USA

ARTICLE INFO

Article history:

Received 29 March 2016

Received in revised form

9 May 2016

Accepted 11 May 2016

Available online 12 May 2016

Keywords:

Dye sensitized solar cells

Indole

Co-sensitizers

Acceptors

Density functional theory

ABSTRACT

Herein, we report the molecular design, synthesis and photovoltaic performance studies of three new organic co-sensitizers, **N₁₋₃** carrying indole and thiophene units linked to different acceptors/anchoring groups, as co-adsorbents for dye sensitized solar cells. We present the role of anchoring/acceptor units on co-sensitization properties **N₁₋₃**. Their photo-physical and electrochemical results along with molecular geometry, obtained from Density Functional Theory are utilized to rationalize the influence of co-sensitizer structures on photovoltaic properties for DSSCs. We have shown that, the co-sensitization effect is profoundly dependent upon the anchoring/acceptor unit in the co-adsorbents. Among them, **N₃** containing 4-aminobenzoic acid shows promising co-sensitization results and exhibits an enhanced efficiency of 9.26%, when co-sensitized with a ruthenium dye, **HD-14**. Further, the study highlights the importance of molecular matching between the sensitizer and co-sensitizer in enhancing the efficiency. Furthermore, vertical electronic excitations are calculated using time dependent density functional theory studies.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The need to generate clean yet viable energy is one of the most important scientific and technological challenges in the 21st century. Due to the possibility of low-cost conversion of photovoltaic energy into electricity, dye-sensitized solar cells (DSSCs) have engrossed great interest in material science throughout the past two decades [1]. Although, sensitizers based on ruthenium complexes have delivered high efficiency (~11%) [2,3], they are hammered by their high cost, low molar extinction coefficient, limited availability of the noble metal and environmental side-effects etc. Due to the aforementioned limitations, scientists across the globe have been forced to look for an alternative to the ruthenium complexes and thereby, designing novel and efficient sensitizers for DSSC application has become exceedingly

imperative. In this regard, metal-free sensitizers have shown a lot of promise [4,5]. The major drawback with metal-free dyes is their lower overall efficiency as compared to metal-based counterparts. The primary reason for the lower efficiency is the faster charge recombination between the injected electrons in the titanium dioxide and the oxidized species present in the electrolyte. On the other hand, the merits of metal-free sensitizers include, facile synthesis, high molar extinction coefficients, cost effectiveness and they are appropriate for large scale application of DSSCs. The challenge is to strike a balance between these two aforementioned aspects. Many researchers around the globe have focused on extending the absorption spectrum of the sensitizer and thereby enhancing the overall efficiency [6]. The main dye design philosophy implemented by various research groups to broaden the absorption spectra of the sensitizers is donor- π -bridge-acceptor (D- π -A) design strategy [7]. However, the extension of absorption spectrum comes with its share of parallel limitations. Firstly, red-shifting the absorption spectrum by extending the conjugation may result in sensitization problems, i.e. dye aggregation on the semiconductor surface, leading to lower photo-conversion

* Corresponding author.

** Corresponding author.

E-mail addresses: avachem@gmail.com, avadhikari123@yahoo.co.in, avachem@nitk.ac.in (A.V. Adhikari).

efficiency. Further, it has been reported that extending the π -conjugation of the sensitizer to absorb the near-IR photons can negatively affect its overall efficiency and stability [8]. Secondly, as a result of broadening of the absorption spectrum, a destabilization of the ground state oxidation potential (GSOP) and/or the excited state oxidation potential (ESOP) is required, which decreases the electron injection and dye regeneration thermodynamic driving forces. Because of these limitations, it still remains a challenge for the scientific community to design highly efficient sensitizers. One of the key tactics deployed to obtain high efficiency for DSSCs is to amend organic dyes in a systematic fashion by changing the crucial constituents or substituents, since minor structural changes to the sensitizers may result in substantial effect on the absorption spectrum as well as interfacial recombination of the sensitizer upon anchoring onto TiO₂ surface.

Keeping all these facts in mind, a viable strategy for enhancement of the overall efficiency of DSSCs is the development of new organic compounds which can be used as co-adsorbents in ruthenium based DSSCs [9–16]. Hence, infusing the merits of both ruthenium based as well as metal-free sensitizers into same DSSC, it is possible to further enhance the overall efficiency of the cell. Generally, the prerequisites for a molecule to act as an ideal co-adsorber are (i) the molecule should possess structural features to avoid competitive adsorption among the sensitizer molecules while efficiently suppressing the dye aggregation on the semiconductor surface, (ii) the co-adsorbents must possess a very high molar extinction coefficient (ϵ) around 400 nm to recuperate the drop in the IPCE spectra due to tri-iodide species present in the electrolyte, and (iii) it should be capable of forming a compact molecular monolayer on the TiO₂ surface and thereby reducing the electron recombination in the TiO₂ film with the redox species present in electrolyte as well as other acceptor species [17].

With the aforementioned points in mind, in the present work we report the design, synthesis, characterization and photovoltaic performance studies of three novel co-adsorbents (**N₁₋₃**) having an indole core and thiophene π -bridge attached to different acceptor units, leading to the formation of **N₁₋₃**. We have used these co-adsorbents to enhance the IPCE spectra by counteracting the competitive light absorption due to triiodide species in 400–500 nm range of the visible spectrum. Further, it was shown that, incorporation of electron-withdrawing and donating groups into the sensitizer molecule enhances the charge-transfer characteristics of absorption spectra and thereby giving a wider and higher absorptivity. In the present work, indole was chosen as the core moiety primarily due to its exceptional electron donating ability and excellent light capturing capability [18,19]. Further, Greenwald et al. reported that by incorporating electron acceptors such as a nitro group in the sensitizer, the photo-currents in photovoltaic devices can be enhanced [20]. Furthermore, it was reported that incorporation of cyanovinylene segment increased the electrochemical stability of the molecule. Also, the presence of cyanovinylene is known to destabilize the ESOP of the sensitizer and thereby bringing about smaller E_{0-0} , and hence resulting in broadening of the absorption spectrum. Against this background, cyanovinylene has been incorporated in the present design. Moreover, we have introduced hexyl chains in all the three co-adsorbents, **N₁₋₃** to fine-tune the distance between ruthenium based sensitizer **HD-14** [21] molecules in order to avoid dye aggregation and to improve the overall efficiency of the cell. Fig. 1 depicts the chemical structures of all the co-sensitizers as well as ruthenium based sensitizer **HD-14**.

In addition, anchoring groups are indispensable in DSSCs as they are essential in grafting the dye into the semiconductor surface, and thereby assisting in achieving better electron injection from the excited state of the sensitizer into the TiO₂ conduction band edge.

Consequently, the way in which the sensitizer is anchored on the semiconductor surface plays a crucial role in determining the efficiency of the electron-injection step at the dye-semiconductor interface. Keeping this in view, we have used three different anchoring groups in the present study and investigated their effect on the co-adsorbing properties as well as overall efficiency of the cell.

2. Experimental

2.1. Materials and methods

The starting materials 5-nitro-1*H*-indole, thiophene-2-acetonitrile, 1-bromohexane, cyanoacetic acid, rhodanine-3-acetic acid and 4-aminobenzoic acid were procured from Sigma-Aldrich and were used without any further purification unless stated otherwise. Ruthenium based sensitizer **HD-14** was synthesized as per the literature [21]. All the solvents were freshly distilled prior to use. All the reactions were performed under argon atmosphere and the progress of reactions was monitored by TLC technique. Chromatographic separations were carried out using silica gel (100–200 mesh). ¹H NMR and ¹³C NMR spectra were recorded from a Bruker avance 500 MHz and 400 MHz spectrometers, using DMSO-*d*₆ or CDCl₃ as solvents and TMS as an internal standard. Further, the fluorescence spectra were run using Perkin Elmer LS55 fluorescence spectrophotometer and UV-visible spectra of the dyes were recorded at room temperature using SPECORD S 600 spectrophotometer. The FTIR spectra were obtained using Nicolet Avatar 5700. The cyclic voltammetry (CV) and impedance measurements were performed on a Bio-Logic SP-150 electrochemical workstation. CV measurements were carried out in acetonitrile by using [0.1 M (*n*-Bu)₄N⁺(ClO₄)⁻] as a supporting electrolyte. The CV experiments were conducted by following the three electrode system, consisting of platinum as counter and Ag/AgCl as a reference electrode and glassy carbon was used as the working electrode. The data were recorded at a scan rate of 100 mV⁻¹. Mass spectra were recorded on thermo scientific-EXACTIVE (ESI-MS), whereas the elemental analysis was carried out on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). Photocurrent-voltage characteristics of DSSC's were measured using a Keithley 2400 source meter under illumination of AM 1.5 G solar light from solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel, 91150V) to set 1 Sun (100 mW cm⁻²). The measurements were fully controlled under Oriel IV Test Station software.

IPCE (incident monochromatic photon to current conversion efficiency) experiments were carried out using a system (QEX10, PV Measurements, USA) equipped with a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source connected to a monochromator. Calibration of incident light was performed before measurements using a silicone photodiode (IF035, PV Measurements). All the measurements were carried out without the use of anti-reflecting film. The electrochemical impedance spectra were measured with an impedance analyzer potentiostat (Bio-Logic SP-150) under illumination using a solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). EIS spectra were recorded over a frequency range of 100 mHz–200 kHz at 298 K. The applied bias voltage was set at the V_{oc} of the DSSCs, with AC amplitude set at 10 mV. The electrical impedance data were fitted using Z-Fit software (Bio-Logic). The procedure for DSSC fabrication is given in supporting information. The DFT calculations were performed using Turbomole software package.

Download English Version:

<https://daneshyari.com/en/article/175349>

Download Persian Version:

<https://daneshyari.com/article/175349>

[Daneshyari.com](https://daneshyari.com)