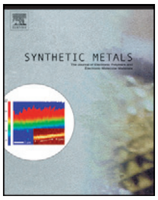
Synthetic Metals 159 (2009) 1028–1033

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Co-sensitization with near-IR absorbing cyanine dye to improve photoelectric conversion of dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 4 September 2008
Received in revised form 13 January 2009
Accepted 15 January 2009
Available online 24 February 2009

Keywords:
Cyanine dye
Co-sensitization
Dye-sensitized solar cell
Photovoltaic properties

ABSTRACT

Two carboxylated cyanine dyes, 3-butyl-2-[3-(1-butyl-5-carboxy-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)-1-propen-1-yl]-1,1-dimethyl-7-[1-[2-[6-(4-morpholinyl)-1,3-dioxo-1H-benz[*de*]isoquinolin-2(3H)-yl]ethyl]-1H-1,2,3-triazol-4-yl]-1H-Benz[*e*]indolium iodide (A), 2-[5-(1-butyl-5-carboxy-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)-1,3-pentadienyl]-3-ethyl-1,1-dimethyl-1H-Benz[*e*]indolium iodide (B), have been prepared and their photophysical and electrochemical properties have been investigated. A, B and their mixtures (AB) were used as sensitizers in nanocrystalline TiO_2 solar cells to improve photoelectric conversion efficiency. It was found that the solar cell sensitized with A3B1 (molar ratio: A:B = 3:1) generated a high power conversion efficiency of 3.0% under AM1.5G illumination (100 mW cm^{-2}), indicating that co-sensitization is a promising method to improve the photoelectrical properties of dye-sensitized solar cells.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted intense interest for their high performance in converting solar energy-to-electricity at low cost. The Ru complex photosensitizers such as the black dye show record solar energy-to-electricity conversion efficiency of 11% [1,2]. Recently, organic DSSCs have received more and more attention for their variety, high molar extinction coefficients, and simple preparation process of low cost in comparison to Ru complexes. Great progress has been made in this field and the highest overall photoelectric conversion efficiency of solar cells sensitized by organic dyes has reached 9%, indicating the promising perspective of metal-free organic dyes [3–26].

In spite of these achievements, the key drawback for most pure organic-based sensitizers is their lack of absorption in the red region of the visible spectrum. The solar spectrum at the earth's surface extends into the near-IR, and the best dyes such as N3 could typically give high-efficiency energy conversion up to only about 600 nm [27]. To overcome this drawback, the synthesis of organic dye with broader absorption spectrum for the DSSCs is a new hot spot. In addition, making use of the complementary absorption spectrum of different pure organic dyes in DSSCs can also improve the properties of DSSCs. Ehret et al. [28,29] studied the nanocrystalline TiO_2 solar cell sensitized by various di-carboxylated cyanines and found that the use of mixed cyanine dyes could improve photoelectric conversion efficiency. Grätzel et al. [30] examined the effects of the mixtures of porphyrines and phthalocyanines applied to nanocrystalline TiO_2 films, they reported that there was no negative interference between the coabsorbed chromophores and the result obtained was encouraging. Guo et al. [31] investigated the nanocrystalline TiO_2 solar cells co-sensitized with novel cyanine dyes and found that cyanine dyes aggregates could harvest light efficiently. The group of Zhang used a combination of three organic dyes, with absorption maxima at 380, 535 and 642 nm, to achieve a higher efficiency than any of the individual dyes alone [32]. Recently, Grätzel and coworkers combined bisthiophene dye (JK2) with squarylium cyanine dye (SQ1) as co-sensitizers and got an overall conversion efficiency of 7.43% [33]. Moreover, they also used zinc phthalocyanine (TT1) and JK2 as co-sensitizers and gave an overall cell efficiency of 7.74%, which is higher than either of the two dyes alone. These works have shown a clear advance towards efficient co-sensitized DSSCs based on systems with extended spectral response in the near-IR region [34].

Although some progresses in the co-sensitization of nanocrystalline TiO_2 with organic dyes have been achieved, further investigating the co-sensitization properties of DSSCs with different organic dyes is still needed. Cyanine dyes have very high absorption extinction coefficients (~10^5 M^{-1} cm^{-1}), intense and broad absorption band in visible and near-infrared region, and excellent sensitizing properties in photography. Especially, cyanine dyes adsorbed on the nanocrystalline TiO_2 film can form *J*- or *H*-aggregates, which contributed to hypsochromism and bathochromism, respectively. Relative high incident photo-to-electron conversion efficiency (IPCE) values are expected over a

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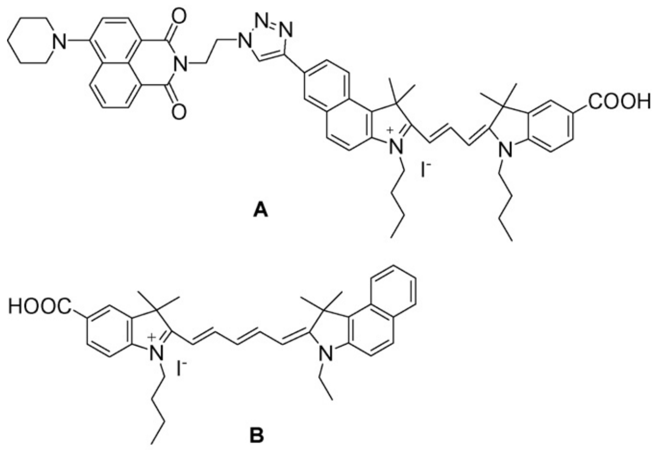
doi:10.1016/j.synthmet.2009.01.023



Scheme 1. Molecular structures of A and B.

wider region of wavelength, which then will in turn enhance the conversion efficiency of light to electricity.

In this paper, a trimethine cyanine dye (A) and a near-IR absorbing pentamethine cyanine dye (B) (Scheme 1) were selected as co-sensitizer. The presence of two butyl chains on indole nucleus can improve the solubility and form a tightly packed insulating monolayer, preventing the I_3^- or cations from approaching the TiO_2. The sensitizing properties of five mixed dyes with different A-to-B ratios were systematically studied due to their complementary photoresponse. It was found that the mixtures of the two dyes could be employed to co-sensitize the solar cell over the entire visible spectrum and the solar-cell performance was improved. The effects of the co-adsorption of compounds A and B on photosensitization properties are investigated as well.

2. Experimental

2.1. Materials

The FTO conducting glass (fluorine doped SnO_2, sheet resistance <15 Ω/square, transmission >90% in the visible) was obtained from Geao Science and Educational Co. Ltd., China. 3-Methyl-2-oxazolidinone and lithium iodide were purchased from Sigma–Aldrich. All other solvents and chemicals (reagent grade) were supplied by Sinopharm Chemical Reagent Co., Ltd., China and used as received. Compound A was synthesized according to the reference [35]. The synthetic route of compound B is shown in Scheme 2 and the detailed experimental procedures and characterization data are given below.

3-Ethyl-1,1,2-trimethyl-1H-benzo[*e*]indolium iodide (3 g, 8.2 mmol) and N-[(E)-3-(phenylamino)allylidene]benzenaminium chloride (2.12 g, 8.2 mmol) were stirred in acetic anhydride (50 mL) at 100 °C for 2 h. After cooling down to room temperature, the solution was poured into 200 mL ethyl acetate. The precipitate was then filtered and used in the next step without further purification.

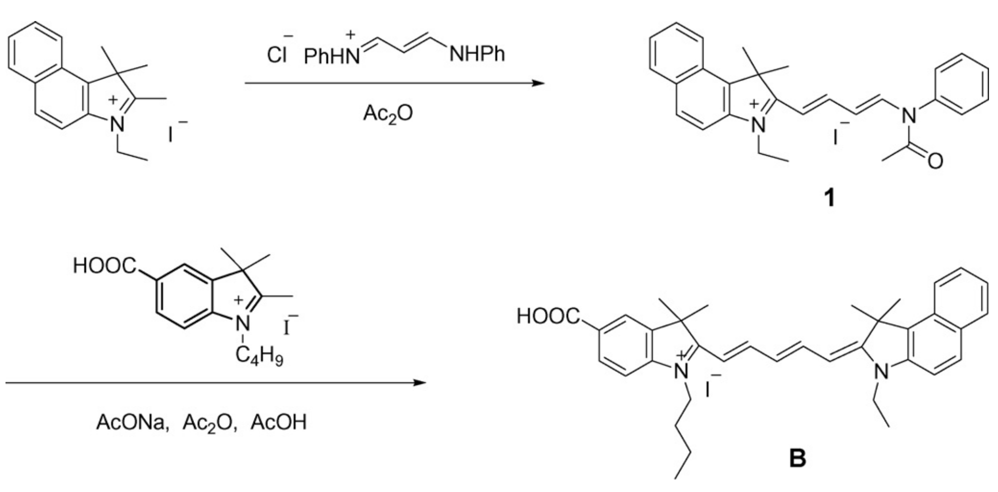
1-Butyl-5-carboxyl-2,3,3-trimethyl-3*H*-indolium iodide (0.41 g, 1.06 mmol), 3-ethyl-1,1-dimethyl-2-[(1E,3E)-4-(N-phenylacetamido)buta-1,3-dienyl]-1*H*-benzo[*e*] indolium iodide (0.57 g, 1.06 mmol) and sodium acetate (0.44 g) were added into 0.4 mL acetic acid and 2.8 mL acetic anhydride. The above mixtures were stirred at 100–110 °C for 1 h and the solution turned into dark blue gradually. Then the mixture was overnight in the refrigerator and precipitate was observed. The precipitate was filtered and purified by column chromatography on silica (*N*,*N*′-dimethylformamide/ethanol = 50:1 v/v) to yield B as blue solid (yield, 75%).

Compound A. ^{1}H NMR (DMSO-d_6, 400 MHz), δ: 8.75 (s, 1H), 8.50 (m, 3H), 8.38 (m, 3H), 8.19 (d, J = 8.8 Hz, 1H), 8.05 (m, 2H), 7.95 (d, J = 8.4 Hz, 1H), 7.75 (m, 2H), 7.35 (d, J = 8.40 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 6.5 (m, 2H), 4.8 (t, J = 5.32 Hz, 2H), 4.50 (t, J = 6.1 Hz, 2H), 4.20 (m, 4H), 3.20 (t, J = 4.7 Hz, 4H), 2.0 (s, 6H), 1.75 (m, 16H), 1.4 (m, 4H), 0.95 (m, 6H); ^{13}C NMR (DMSO-d_6), δ: 175.0, 174.7, 170.31, 164.4, 163.8, 157.7, 149.4, 146.9, 142.2, 139.4, 139.3, 138.1, 133.4, 133.0, 132.1, 131.3, 133.1, 130.0, 127.7, 127.4, 126.2, 125.3, 123.9, 122.4, 121.1, 114.9, 114.6, 111.1, 109.6, 103.1, 102.1, 54.4, 50.8, 49.2, 48.0, 44.5, 39.6, 29.8, 29.6, 27.9, 27.7, 26.1, 24.2, 20.2, 13.9, 13.8; MS(EI):907.4 (M − I$^-$).

Compound B. ^{1}H NMR (DMSO-d_6, 400 MHz), δ: 8.56 (m, 1H), 8.31 (m, 2H), 8.15 (m, 2H), 7.92 (m, 2H), 7.75 (m, 1H), 7.55 (m, 1H), 7.42 (d, J = 8 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 6.72 (m, 1H), 6.58 (m, 1H), 6.22 (d, J = 3.3 Hz, 1H), 4.38 (m, 2H), 4.04 (m, 2H), 1.98 (s, 6H), 1.75 (m, 2H), 1.72 (m, 6H), 1.65 (m, 2H), 1.40 (m, 3H), 0.98 (m, 3H); ^{13}C NMR (DMSO-d_6), δ: 13.02, 14.20, 19.92, 21.83, 26.97, 27.80, 29.41, 41.59, 41.80, 42.01, 43.51, 48.62, 51.60, 103.20, 104.40, 110.13, 112.06, 122.65, 123.56, 125.62, 126.55, 127.94, 128.32, 130.40, 130.57, 130.94, 132.04, 134.51, 139.46, 140.74, 144.90, 153.26, 154.51, 171.79, 175.37; MS(EI):532.3 (M − I$^-$).

2.2. Preparation of dye-sensitized nanocrystalline TiO_2 electrodes

TiO_2 colloidal dispersion was prepared according to the reference [1] using commercial available TiO_2 (P25, Degussa AG, Germany). Nanocrystalline TiO_2 films were prepared by drop cast-



Scheme 2. The synthetic procedures of the cyanine dyes (B).