Photovoltaic performance of dye-sensitized solar cell based on eosin-Y photosensitizer and quasi-solid state electrolyte

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ABSTRACT

Dye-sensitized solar cells (DSSCs), as low-cost photovoltaic devices compared to the silicon based solar cells, have received extensive attention recently; although much work is necessary to reach optimal device efficiencies. This paper reports the fabrication and characterization of dye sensitized solar cells using TiO_2 sensitized by eosin-Y. The electrodes, electrolyte (I^-/I_3^-), and dyes were assembled into a cell and illuminated by a light with an intensity 100 $mWcm^{-2}$ to measure the photoelectrochemical parameters of the prepared DSSCs. According to the experimental results, the maximum quantum efficiency appeared at the wavelength of 510 nm with IPCE of 64.2%. The short circuit current density (J_{SC}), the open circuit voltage (V_{OC}), and power conversion efficiency (η%) were measured to be 6.4 $mAcm^{-2}$, 0.54 V, and 2.2%, respectively. The result of UV-visible absorption and IPCE measurement showed that the IPCE correlated to the absorption spectrum of the active layer. The IPCE and η% obtained in the present work was higher than the values reported earlier for the liquid state electrolyte system indicating that the quasi-solid-state electrolyte could substitute the liquid state.

Keywords: Dye sensitized solar cells, Eosin-Y, Quasi-solid-state electrolyte.
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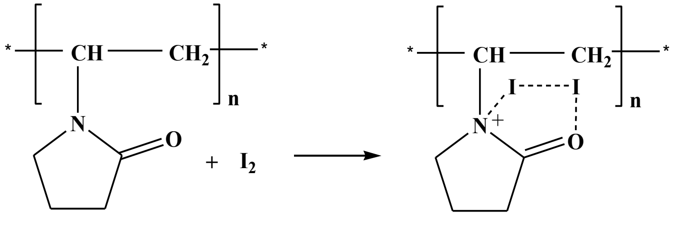
INTRODUCTION

While the Dye sensitized Solar Cells (DSSCs) have attracted much attention in the recently, still the long-term stability and the use of expensive dyes are some of the major draw backs of these solar cells in popularizing them in the practical applications. Thus far, the most efficient DSSCs are made using ruthenium dye complexes; with power conversion efficiency record of about 12% with the illumination of 100 $mWcm^{-2}$ (AM 1.5) (Nazeeruddin *et al.*, 2005; Hagfeldt *et al.*, 2010; Nazeeruddin *et al.*, 2011). The dependability factor implies the robustness of the device to maintain a reasonable performance after long term exposure to weathering elements.

Dye-sensitized solar cell (DSSC) composed of dye-sensitized nanometer porous TiO_2 film, electrolyte containing iodide/triiodide (I_3^-/I^-) redox couple, and counter electrode has attracted worldwide attention because of its low production cost and potential alternative to traditional photovoltaic devices (O'Regan and Grätzel, 1991; Nazeeruddin *et al.*, 1993). DSSC based on liquid electrolyte containing acetonitrile as organic solvent, has an overall light-to-electricity conversion efficiency of 11% under irradiation of AM1.5 (Grätzel, 2004). However, liquid-junction cell remains as a problem in low long-term stability, which is caused by organic solvent evaporation and leakage, high temperature instability, and difficulties in sealing (Smestad *et al.*, 2003).

To overcome these problems, much effort has been made to replace liquid electrolytes with ionic liquids (Wang *et al.*, 2003a; Kuang *et al.*, 2006; Bai *et al.*, 2008; Chuan *et al.*, 2017), solid or quasi-solid state electrolytes including polymer gel electrolytes (Katsaros *et al.*, 2002; Stathatos *et al.*, 2003; Kim *et al.*, 2005; Wu *et al.*, 2007; Meidan *et al.*, 2015), p-type semiconductors (Kumara *et al.*, 2002; O'Regan *et al.*, 2002; Meidan Y. *et al.*, 2015), and organic conductive materials (Krüger *et al.*, 2002; Zafer *et al.*, 2005). Ionic liquids, such as imidazolium salts, have received attention because of their remarkable properties, including non-volatility, chemical and thermal stability, and high ionic conductivity (Wang *et al.*, 2003a; Bai *et al.*, 2008). On the other hand, substituting liquid electrolyte with the polymer gel electrolyte has been considered as offering several advantages compared with the original wet cells. Research on matrix materials solidifying liquid electrolytes has also been undertaken to improve the leakage durability of liquid electrolytes. Furthermore, ionic gels and ionic polymer electrolytes prepared by incorporating ionic liquid electrolytes into matrix materials have been investigated to avoid the leakage and improve evaporation durability of the electrolytes (Wang *et al.*, 2002; Stathatos *et al.*, 2003; Wang *et al.*, 2003b; Chen *et al.*, 2007). Figure 1 shows the device structure and operating principle of the dye sensitized solar cell.

In this paper, dye sensitized solar cell was fabricated using eosin-Y dye as sensitizer and a quasi-solid state electrolyte composed of novel polymer electrolyte based on Polyvinyl pyrrolidone (PVP), an ionic liquid 1-ethyl-3-methylimmidazolium iodide (EMIm-I), sodium iodide (NaI), iodine (I_2) and poly(3,4-ethylenedioxythiophene) (PEDOT). PVP deserve a special attention because of good environmental stability, easy processability, moderate electrical conductivity and rich information in charge transport mechanism (Reddy *et al.*, 2006). Figure 2 shows the chemical structure of eosin-Y, PVP, EMIm-I and PEDOT. PVP is also a nitrogen-containing heterocyclic polymer, which can form $PVPI_2$ by reaction with I_2 (Eq. (1)) (Hugo and Newton, 1963).



(1)

It has been demonstrated well that N-containing heter ycles can enhance the open-circuit photovoltage (V_{OC}) of the solar cell (Kusama *et al.*, 2005).

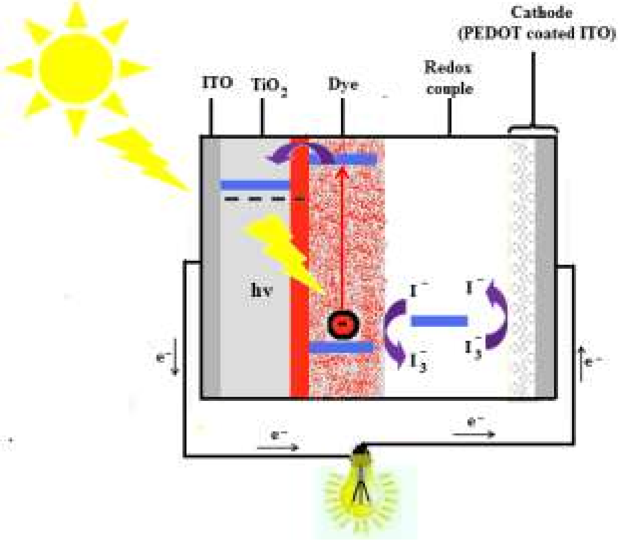


Figure 1. The device structure and operating principle of the dye sensitized solar cell.

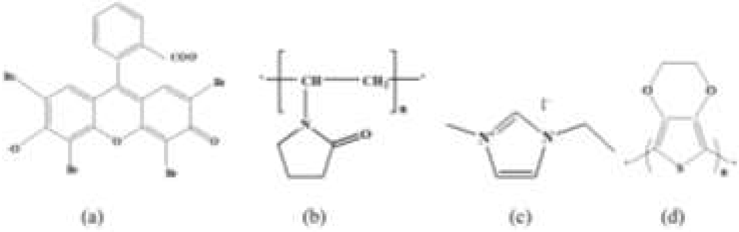


Figure 2. The Chemical structure of (a) eosin-Y (b) PVP (c) EMIm-I and (d) PEDOT.

MATERIALS AND METHODS

ITO-coated glass having transmittance above 80% in the visible region of the solar spectrum was employed as a substrate for the photoactive materials and counter electrodes. It was cleaned in ultrasonic bath successively with acetone (Aldrich), 2-propanol

(Riedel-de Haen), and ethanol (BDH) and dried with an air gun for 10 minutes in each step.

Preparation of mesoporous TiO_2 film was done with the method described elsewhere (Nazeeruddin *et al.*, 1993). Briefly: 3 g of TiO_2 (P25, Degussa) powder was ground in a porcelain mortar with 1 mL water containing 0.1 mL acetylacetone to prevent reaggregation of the particles. After the powder had been dispersed by the high shear forces in the viscous paste, it was diluted by slow addition of 4 mL water under continued grinding. Finally, a detergent 0.05 mL Triton X-100, (Aldrich) was added to facilitate the spreading of the colloid on the substrate. The ITO was covered on two parallel edges with adhesive tape to control the thickness of the TiO_2 film and to provide noncoated areas for electrical contact. The colloid was applied to one of the free edges of the conducting glass and distributed with a glass rod sliding over the tape-covered edges. After air drying, the electrode was fired for 30 min at 450 in a furnace (Carbolite Model ELF 11/14B).

Sensitizing of the TiO_2 with dye was carried out by soaking the film for 2 h in a 0.3 mM solution of eosin-Y dye (Aldrich) in dry ethanol. The dye sensitizing was done immediately after the high temperature annealing while still hot in order to avoid rehydration of the TiO_2 or capillary condensation of water vapor from ambient air inside the nanopores of the film (Nazeeruddin *et al.*, 1993). The presence of water in the pores decreases the injection efficiency of the dye. After completion of the dye adsorption (Nazeeruddin, *et al.*, 1993), the electrode was withdrawn from the solution under a stream of dry air. It was stored in dry ethanol or immediately wetted with redox electrolyte solution for fabrication of DSSC.

The polymer film for the counter electrode was obtained by electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) (Aldrich), in a three electrode one-compartment electrochemical cell. The electrochemical cell consisted of a pre-cleaned ITO-coated glass working electrode, platinum foil counter electrode and quasi-Ag/AgCl reference electrode. The solution used for the polymerization contained 0.2 M EDOT and 0.1 M $(C_2H_5)_4NBF_4$ (Aldrich) in acetonitrile (Aldrich). The monomer was used as received. The polymerization was carried out potentiostatically at +1.8 V for 2 seconds. At this potential, the electrode surface becomes covered with blue-doped PEDOT film. The PEDOT covered ITO glass was then rinsed with acetonitrile and air dried.

The polymer gel electrolyte was prepared as reported in reference (Fan *et al.*, 2010) and 0.9 M of EMIm-I was added into acetonitrile under stirring to form a homogeneous liquid electrolyte. In order to obtain a better conductivity, 0.5 M of sodium iodide (BDH) was dissolved in the above homogeneous liquid electrolyte, and then 0.12 M iodine and 35% (w/w) of PVP were added. Then, the resulting mixture was heated at 70 – 80 °C under vigorous stirring to dissolve the PVP polymer, followed by cooling down to room temperature to form a gel electrolyte. Finally, the gel electrolyte was deposited in the form of thin film on top of the dye coated TiO_2 electrode. The photoelectrochemical cell (PEC) was completed by pressing against PEDOT-coated ITO glass counter electrode which was prepared electrochemically with a procedure described above. The PEC was then mounted in a sample holder inside a metal box with an area of 1 cm^2 opening to allow light from the source. The photoelectrochemical measurements of the cell were performed using a computer controlled CHI630A Electrochemical Analyzer. A 250-W tungsten-halogen lamp regulated by an Oriel power supply (Model 68830) was used to illuminate the PEC. A grating monochromator (Model 77250) placed into the light path was used to select a wavelength between 300 and 800 nm. The measured photocurrent spectra were corrected for the spectral response of the lamp and the monochromator by normalization to the response of a calibrated silicon photodiode (Hamamatsu, Model S1336-8BK) whose sensitivity spectrum was known. No correction was made for the reflection from the surface of the sample. The white light intensity was measured in the position of the sample cell with Gigahertz-Optik X11 Optometer. A series of neutral density filters were used to vary the incident light intensity on the sample. The optical absorption spectrum of the film was measured using UV-Vis spectrometer (Spectroscopic GENESYS 2PC. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

UV-visible absorption spectra of eosin-Y in ethanol solution and eosin-Y adsorbed on TiO_2

While Figure 3(a) depicts the UV–Vis absorption of eosin-Y solution in ethanol, Figure 3(b) presents the UV-Vis absorption of eosin-Y adsorbed onto TiO_2 electrode. An absorption peak of photoanode was broader than that of the dye solution (Figure 3(b)), with a shift to a higher wavelength (from 510 to 525 nm). The difference in the absorption peak was due to the binding of eosin-Y to the oxide surface (Vinodgopal *et al.*, 1995; Muhammad *et al.*, 2019).

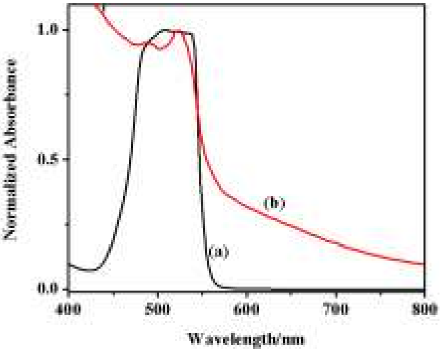


Figure 3. Light absorption spectra of (a) dye solution in ethanol and (b) dyes adsorbed on TiO_2.

Photoelectrochemical measurements

The photocurrent density -voltage (J-V) characteristics of the DSSCs constructed with eosin Y coated photoanode, PEDOT coated ITO counter electrode and polymer gel electrolyte with redox couple, measured under AM 1.5, 100 mW cm^{-2} illuminations are shown in Figure 4. From the analysis of the J-V curves, important photovoltaic parameters for the DSSC including (1) the open-circuit voltage, V_{OC}; (2) the short circuit photocurrent density, J_{SC}; (3) the fill factor (FF); and (4) the cell's overall energy conversion efficiency (η) was obtained. The cell's fill factor was estimated according to Eq. (2) (Yang *et al.*, 2011):

$$FF = \frac{V_{mp}J_{mp}}{V_{OC}J_{SC}} \tag{2}$$

where V_{mp} and J_{mp} are the voltage and the current density, respectively for the maximum power output. Taking into account the FF parameters, the energy conversion efficiency was calculated following Eq. (3) (Yang *et al.*, 2011):

$$\eta(\%) = \frac{V_{OC}J_{SC}FF}{P_{in}} \times 100 \tag{3}$$

As it is depicted in Figure 4, while the short circuit current density (J_{SC}) and the open circuit voltage (V_{OC}) were measured to be 6.37 mAcm^{-2} and 0.54 V, respectively, the power conversion efficiency (η%) was calculated to be 2.17%. The fill factor, which is the measure of the squareness of the output characteristics, was also calculated to be 63%. Comparison of the photoelectrochemical performance of the present eosin-Y dye based DSSC in terms of short circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and energy conversion efficiency (η) against some previous reports is shown in Table 1.

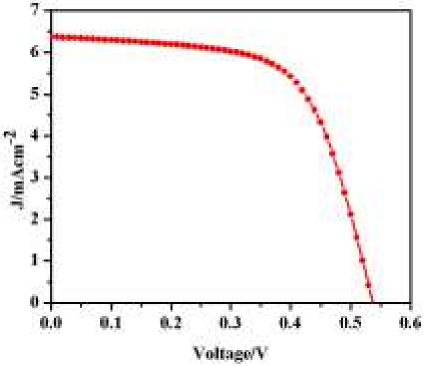


Figure 4. J-V characteristics curve for eosin-Y based quasi-solid state DSSC.

UV-visible absorption spectrum of eosin-Y/TiO$_2$ and photocurrent action Spectrum of the DSSC

The photocurrent collected at a different wavelength, relative to the number of photons incident on the surface at that wavelength, determines the spectral response of the device sometimes known as the external quantum efficiency or collection efficiency at each wavelength. Light of different wavelengths is absorbed at different depths in the TiO_2/dye photoanode film. The ability of a solar cell to generate photocurrent at a given wavelength of the incident light was measured by the incident monochromatic photon to current conversion efficiency (IPCE), defined as the number of electrons generated per number of incident photons (Eq. (4)).

$$IPCE\% = \frac{1240[eVnm]J_{SC}[mAcm^{-2}]}{\lambda[nm]I_{in}[mWcm^{-2}]} \times 100 \qquad (4)$$

where J_{SC} is the short-circuit photocurrent density for monochromatic irradiation, and λ and I_{in} are the wavelength and the intensity, respectively, of the monochromatic light. If IPCE is 1, every absorbed photon injects an electron into the circuit. IPCE is a measure for the absorption quality of the solar cell at a certain wavelength combined with its charge transport quality. If the cell absorbs all incident photons at a certain wavelength but the charges cannot travel to the electrodes due to recombination, the IPCE nevertheless will be zero. Hence, the IPCE correlates often to the absorption spectrum of the active layer but a strong deviation cannot be excluded. As can be seen from the UV-visible absorption spectrum of eosin Y adsorbed on TiO_2 electrode (Figure 5(a)) and incident photon to current conversion efficiency (IPCE) curve (Figure 5(b)), the maximum absorbance was observed at 525 nm and IPCE for the device was high (64.17%) at 510 nm.

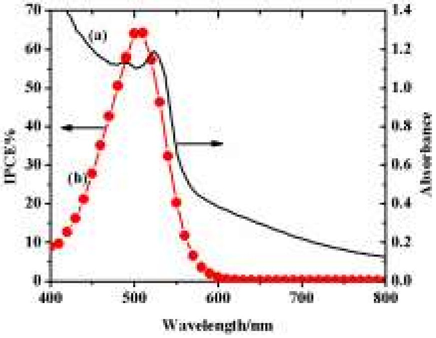


Figure 5. (a) UV-visible absorption spectrum of eosin Y adsorbed on TiO_2 electrode and (b) Photocurrent action spectrum of a quasi-solid state DSSC sensitized by eosin Y dye.

Table 1. Comparison of the photoelectrochemical performance of the DSSCs sensitized by eosin-Y dye with some of the previous reports

Electrolyte	J_{SC} ($mAcm^{-2}$)	V_{OC} (V)	FF (%)	η (%)	References∗
Liquid state	7.4	0.55	52.5	2.16	B
Liquid state	4.0	0.59	61.0	1.43	S
Quasi-solid-state	6.4	0.54	63.0	2.17	T

∗B stands for Baviskar *et al.* 2014, S for Suri *et al.* 2007, and T for the Current study

CONCLUSION

In this study, dye sensitized solar cell was successfully fabricated using eosin-Y dye as sensitizer and a quasi-solid-state electrolyte composed of polymer electrolyte based on PVP, an ionic liquid EMIm-I, NaI and I_2. The maximum value of IPCE of 64.17% at 510 nm obtained in the present work was higher than the values reported earlier. The energy conversion efficiency (η) of the DSSC 2.17% with short circuit current density (J_{SC}) of 6.37 mA cm^{-2}, an open-circuit (V_{OC}) of 0.54 V and a fill factor of 63%, under illumination of 100 mW cm^{-2}, was obtained. The UV-visible absorption measurement result was observed to be consistent with IPCE.

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