



Enhanced Performance of Dye-Sensitized Solar Cells Using Perovskite/DSSCs Tandem Design

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Tandem solar cells were developed for improved efficiency in connection with perovskite solar cells and dye-sensitized solar cells. The organic dye based on thioindigo and N719 were applied in fabricating dye-sensitized solar cells as photosensitizers. We achieved an 8.77% and 10.54% efficiency tandem solar cell formed by a top perovskite solar cell and dye-sensitized solar cells based on organic dye and N719 for the bottom cell, respectively. The photovoltage of tandem solar cells was reported about 1.1 V, but the photocurrent was limited by the dye-sensitized solar cells and was about 12.8 mAcm^{-2} .

Key words: Dye-sensitized solar cells, perovskite, new configuration, efficiency, organic dye

INTRODUCTION

The global energy demand is estimated to increase by 1 GW/day, so energy infrastructure must be developed.¹ Recently, photovoltaic devices such as dye-sensitized solar cells (DSSCs) are greatly considered for generating green energy due to their ease of preparation and being environmentally friendly.² DSSC components are as follows: anode electrode, photosensitizer, electrolyte and counter electrode.³ The performance of DSSCs depends on dye molecules used as photosensitizers due to photo-excitation of dye.⁴ Various photosensitizers including organometallic compounds, organic molecules and natural dyes are prepared and used in the configuration of DSSCs.⁵ The preparation of organic dyes is relatively easy and low cost and doesn't require expensive materials such as ruthenium.⁶ On the other hand, the efficiency of these compounds, especially the indoline and thiophene family, is appropriate in DSSCs.^{7,8} Two organic dyes based on indenol[1,2-b]indole contain thiophen as π -bridges were synthesized by Yan et al. Results showed that the highest efficiency of about 7.99%

was achieved.⁹ A new organic dye based on indoline was prepared by Naik et al. The photovoltaic device fabricated based on this dye displayed efficiency of 3.55%.¹⁰ Despite extensive research to optimize the structure of dye molecules and improve their efficiency in DSSCs, the efficiency of the dye-sensitized solar cells based on organic dye is still low.¹¹ There are two methods, namely co-sensitization and tandem configuration, for achieving high efficiency.^{12–14}

He et al. (1999) reported the first tandem dye-sensitized solar cells (T-DSSCs), followed by the incorporation of T-DSSCs into this photocathode a year after meeting this limitation.¹⁵ Employing the tandem configuration is of significant interest due to its high open-circuit voltage (V_{OC}) and high overall power conversion efficiency.¹⁶ Perovskite-based tandem cells can be used to increase the power conversion efficiency of the device beyond the single junction Shockley–Queisser limit at relatively lower additional costs.¹⁷ In recent years, remarkable attempts have been made to achieve a variety of perovskite-based tandem devices by optimizing some crucial parameters such as band gaps of absorber materials.¹⁶

A preassembled DSSC, hybrid devices and a combination of sensitized photocathodes with sensitized photoanodes are different types of tandem

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configuration.¹⁸ Combining perovskite and DSSCs devices in tandem configuration is new method for improved DSSCs performance. Recently, the perovskite with ABC_3 was employed as general formula in the solar cell preparation, namely perovskite solar cells (PSCs). These devices are economically and environmentally viable renewable technology for the generation of electrical energy.^{19,20} An interesting configuration resulting from the combination of DSSCs and PSCs is highly sought for increasing efficiency.

In this work, a new tandem device from the combination of DSSCs based on thioindigo organic dyes and PSCs were assembled and their efficiencies were compared. The tandem device applied to this method of construction was used for the first time and the main aim was improved efficiency.

EXPERIMENTAL

Materials

All chemical ingredients were bought from Merck Company and used without purification. The preparation path of organic dyes (Fig. 1) is described in a previously published paper.²¹ Transparent conducting oxide, FTO (F-doped SnO_2 , Dye Sol), titanium dioxide (TiO_2) paste, scattering layer and Di-tetrabutylammonium Cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-Ruthenium (II) (N719) were bought from Sharif Solar Company.

Electrochemical Measurements

Electrochemical measurements of the synthesized dye were carried out in acetonitrile. The oxidation potential (E_{ox}) was measured using three small-size electrodes. Ag quasi reference electrode (QRE) was used as the reference. Platinum wires were used as the working and the counter electrodes. All electrode potentials were calibrated with respect to ferrocene(Fc)/ferrocenium (Fc^+) redox couplet. An acetonitrile solution of 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} .²¹

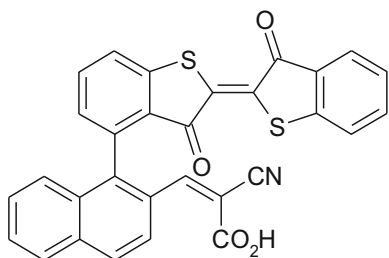


Fig. 1. Chemical structure of the used organic dye.

Fabrication of Solar Cells

In this study, individual DSSCs, PSCs and tandem configuration were prepared for investigation of DSSCs photovoltaic properties.

In individual devices, TiO_2 paste was applied on a fluorine-doped tin oxide (FTO)-glass and was immersed in the dye solution for 20 h at room temperature. Then, the sensitized film was washed with ethanol and was assembled into a sandwich model with a Pt counter-electrode. The sensitized electrode and Pt counter-electrode were assembled into a sandwich-type cell by a $25 \mu\text{m}$ -thick Surlyn hot-melt gasket and sealed by heating.^{22,23}

A 100-nm thin mesoporous TiO_2 was spin coated on top of the bl- TiO_2 /FTO substrate at 1000 rpm for 50 s using homemade TiO_2 pastes. The pristine paste had been diluted in 2-methoxyethanol (1 g/5 mL), and calcinated at 500°C for 1 h in air, which led to a thickness of about 100 nm. The $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ perovskite solutions were then coated onto the mp- TiO_2 /bl- TiO_2 /FTO substrate heated to 50°C by two consecutive spin-coating steps, for 5 s and 10 s at 1000 rpm and 5000 rpm. The $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ (0.8 M) perovskite was obtained by dissolving $(\text{NH}_2)_2\text{CHI}$ (FAI) and $\text{CH}_3\text{NH}_3\text{Br}$ (MABr) with PbI_2 and PbBr_2 in (DMF) and DMSO (6: 1 v/v). The substrate was then dried on a hotplate at 100°C for 10 min. A poly-/toluene solution with an additive of 7.5 mL of Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile and 7.5 ml of 4-tert-butylpyridine (TBP)/acetonitrile was spin-coated on a $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ /mp- TiO_2 /bl- TiO_2 /FTO substrate at for 30 s 3000 rpm. Then, by thermal evaporation, an Au counter-electrode was entrusted.²⁴

In T-DSSCs, dye-sensitized solar cell devices and PSCs were connected as fluorine-doped tin oxide (FTO) glass/ TiO_2 /dye/electrolyte/semi-transparent Pt and PEDOT:PSS-perovskite solar cell structure²⁵ (Fig. 2).

An action spectrum was measured under monochromatic light with a constant photon number ($5 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1}$). J - V characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm^{-2}) through a shading mast ($5.0 \text{ mm} \times 4 \text{ mm}$) by using a Bunko-Keiki CEP-2000 system.

RESULTS AND DISCUSSION

The organic dye was synthesized similar to a method mentioned earlier. The Knoevenagel standard and reduction reaction to LiOH process was employed for dye synthesis.²¹ The purified organic dye was applied on TiO_2 substrate via immersion. The wavelength of maximum absorption (λ_{max}) and the molar extinction coefficients (ϵ_{max}) for organic dye in THF are 498 nm and $36,383 \text{ M}^{-1}\text{cm}^{-1}$, respectively. The wavelength of maximum absorption (λ_{max}) of the synthesized dye on TiO_2 substrate

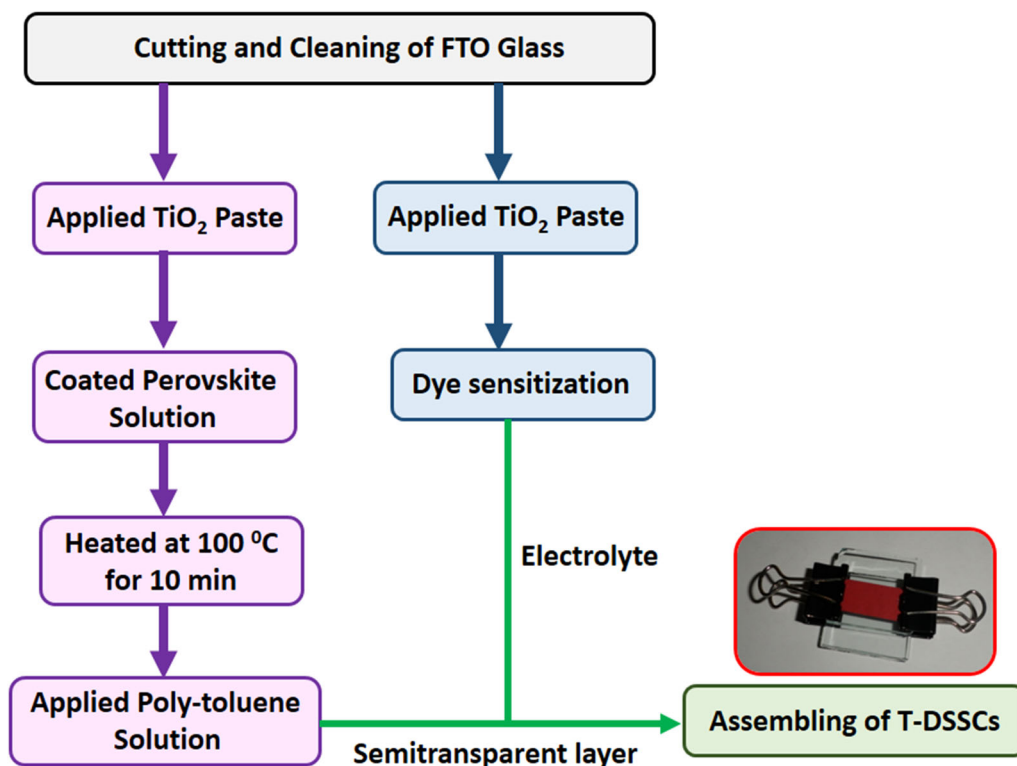


Fig. 2. Flow chart of the T-DSSCs preparation.

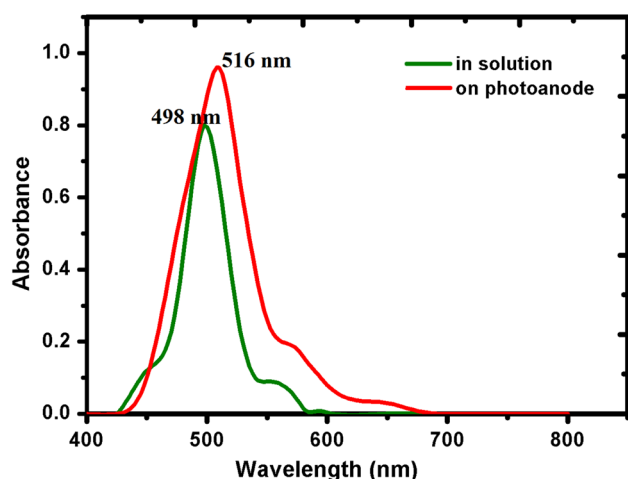


Fig. 3. UV-Visible spectra of organic dye in solution and adsorbed on photoanode.

is 516 nm. The J-aggregation of dye molecules on TiO_2 substrate causes bathochromic shift in the wavelength of maximum absorption; thus, the use of anti-aggregation agents is essential.²⁶ Figure 3 shows the UV-Visible spectra of the dye solution and titanium dioxide substrate sensitized by the dye. An organic dye based on the thioindigo family was used as a photosensitizer.

The oxidation potential (E_{ox}) of organic dye was measured in acetonitrile by cyclic voltammetry. The oxidation peak potential (E_{pa}) for synthesized dye is,

therefore, calculated to be + 0.91 V versus Fc/Fc^+ (as an external standard Ferrocene/Ferrocenium redox couple) in acetonitrile, respectively. The excited-state oxidation potentials of organic dye is -1.3 V and more negative than the conduction band gap edge of TiO_2 [-0.5 V (versus NHE)]. The energy levels of the ground state of photosensitizer (0.91 V) are sufficiently more positive than the I_3^-/I^- redox potential [(0.42 V (versus NHE)], indicating that the oxidized dye formed after electron injection into the conduction band of TiO_2 accepts electrons from I^- ions in the electrolyte, being thermodynamically favorable.^{14,21}

A typical photocurrent-photovoltage ($J-V$) curve for device based on organic dye and Di-tetrabutylammoniumcis-bis (isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) (N719) and IPCE curve of DSSCs are illustrated in Fig. 4. The incident photon-to-electron conversion efficiency (IPCE) value of individual DSSCs is 85.3 that affected the efficiency of DSSCs.^{27,28}

PSC devices are a new technology of solar cell devices that generate low-cost, renewable energy with high absorption,²⁹ superior electron/hole mobility³⁰ and easy processability³¹ is the use of PSCs devices.¹⁹ Perovskite solar cells were prepared by laminating two separated perovskite-based substrates with the structure of FTO/compact TiO_2 (c- TiO_2)/mesoporous TiO_2 (mp- TiO_2)/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ and ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$, which are defined as back sub-cell and front sub-cell, respectively.³² In this work, we prepared PSCs based on the reported

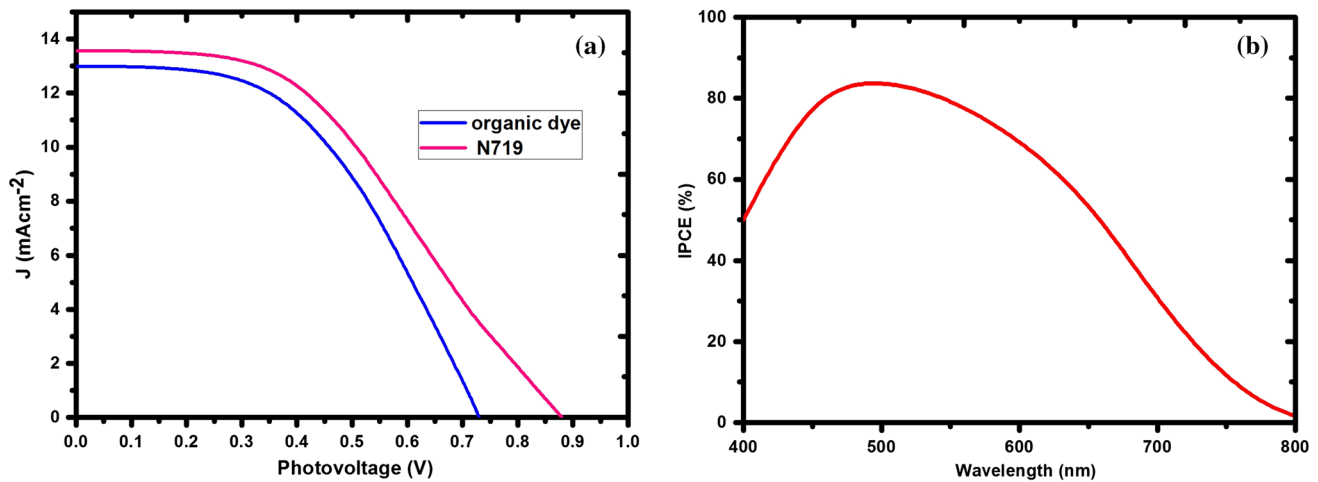


Fig. 4. (a) J - V and (b) IPCE curves of DSSCs.

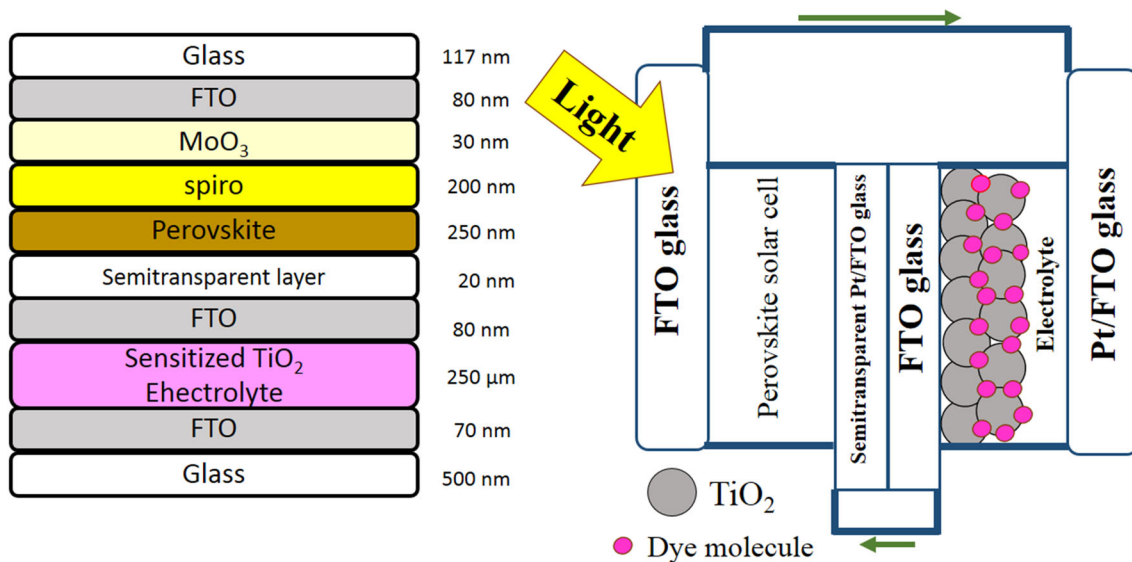


Fig. 5. Schematic illustration of the investigated tandem devices.

method in Kinoshita et al.²⁴ Our PSC showed a V_{OC} of 0.94 V, a J_{SC} of 19.24 mAcm⁻², a fill factor of 0.68 and a power conversion efficiency of 12.3%. Our power conversion efficiency (12.3%) is less than that obtained by Kinoshita et al. (18.4%). This is probably due to the differences in materials and production conditions. Our main goal is to use the PSCs for the preparation of tandem DSSCs/PSCs. Tandem devices illustrate higher efficiency than individual devices due to expanding the spectrum of sunlight.³³ PSCs demonstrate high-efficiency performance and they are an ideal candidate for tandem device preparation.^{30,34} The first perovskite tandem solar cells were assembled in a two-terminal (2T) configuration by Todorov et al. with an efficiency of 4.4%.³⁵ Then, four-terminal (4T) perovskite tandem devices were assembled by Baile.³⁶ The highest efficiency for a 4T device of

about 25.2% was reported by Werner.³⁷ In this study, we designed perovskite/DSSCs tandem solar cells (Fig. 5). In our configuration, the top cell is a perovskite solar cell and the bottom cell is DSSC. Figure 6 shows typical results of the J - V and IPCE curves for PSC/DSSC tandem solar cell. In addition, the photovoltaic parameters are illustrated in Table I.

Standard solar irradiation was employed for studying the efficiency and performance of the photonic device. The research illustrated that changing of the assembly method from individual to tandem configuration devices (contain two types of system) increase power conversion efficiency.^{34,38-40} In this study, the tandem device contains PSCs as top solar cell and DSSCs as bottom solar cell prepared through series connection. Figure 4a schematically illustrates the

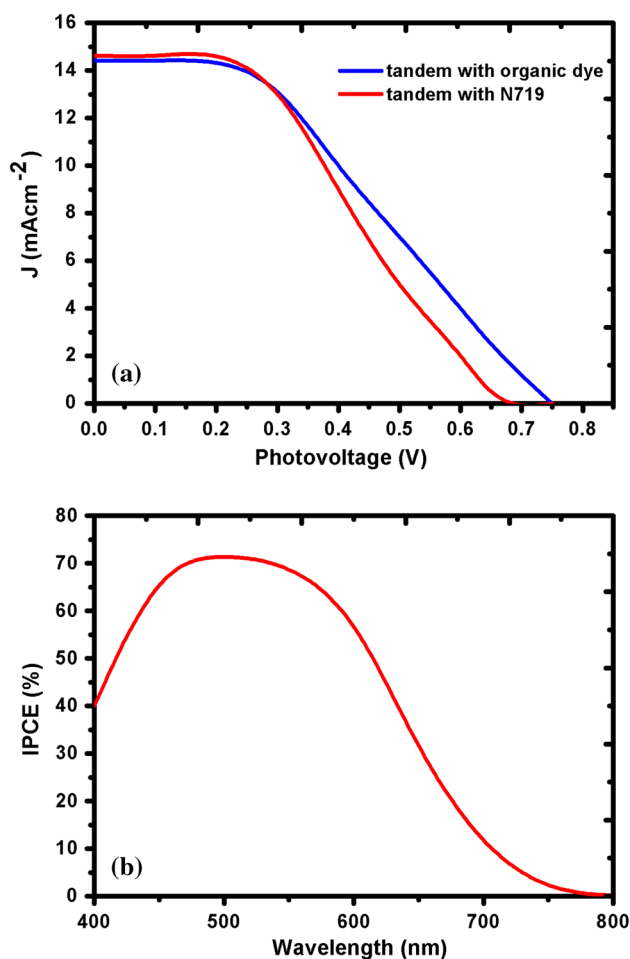


Fig. 6. (a) J - V curve and (b) IPCE of tandem solar cells.

Table I. Photovoltaic parameters of PSC/DSSC tandem solar cell.

Device	J_{sc} (mA cm ⁻²)	V_{OC} (V)	FF (%)	η (%)
DSSC ¹	12.99	0.67	0.68	5.91
PSC	19.24	0.94	0.68	12.3
PSC/DSSC ² tandem	12.11	1.05	0.69	8.77
DSSC ³	13.55	0.88	0.71	8.47
PSC/DSSC ⁴ tandem	12.88	1.17	0.70	10.54

¹individual DSSCs based on organic dye, ²based on organic dye, ³individual DSSCs based on N719 and ⁴based on N719.

preparation of tandem device. In prepared tandem device, two solar cells are connected in series and solar cells containing lower photocurrent controlled the performance of the device. According to the results extracted from the I - V curves of T-DSSCs in

Fig. 4b, the application of tandem configuration resulted in an increase in efficiency compared to the individual DSSCs.

CONCLUSION

Organic dye based on thioindigo and N719 is applied in the fabrication of DSSCs. We assembled a tandem device with a top dye-sensitized solar cell and a bottom perovskite solar cell. The tandem PSCs/DSSCs were fabricated from organic dye for the first time. The photovoltaic properties of all devices increased as expected because V_{oc-tan} is the sum of two V_{oc} of individual DSSCs. The tandem solar cells illustrated a high V_{oc} , but photocurrent was limited by the J_{sc} value of the DSSC bottom cell in a tandem configuration.

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