

Tandem Dye-Sensitized Solar Cells Based on TCO-less Back Contact Bottom Electrodes

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Abstract. Mechanically stacked and series connected tandem dye sensitized solar cells (T-DSSCs) are fabricated in novel architectures. The architecture consist of TCO tandem DSSCs stacked with TCO-less back contact DSSCs as bottom electrodes (TCO-less tandem DSSCs). Resulting TCO-less tandem DSSCs architecture finds its usefulness in efficient photon harvesting due to improved light transmission and enhanced photons reaching to the bottom electrodes. The fabricated tandem performance was verified with visible light harvesting model dyes D131 and N719 as a proof of concept and provided the photoconversion efficiency (PCE) of 6.06 % under simulated condition. Introduction of panchromatic photon harvesting by utilizing near infrared light absorbing Si-phthalocyanine dye in combination with the modified tandem DSSC architecture led to enhancement in the PCE up to 7.19 %.

1. Introduction

Mesoscopic injection solar cells (DSSCs) have emerged an important economical photovoltaic technology with associated advantages of flexibility, colorful and semitransparency. The superior performance at low light intensity make them valuable for interior decorative photovoltaic purposes [1]. Constituents of DSSCs include transparent conductive oxide (TCO) layer, mesoporous TiO_2 layer, sensitizers, electrolytes and catalytic layer. Intense efforts are carried out to enrich photoelectric conversion efficiency (PCEs) and Hanaya et al achieved a mile stone of more than 14% by designing novel sensitizers in spite of the photon harvesting mainly in the visible reason of the solar spectrum [2]. A panchromatic photon harvesting from visible to near infra-red region is, therefore, highly desired to enhance the photoconversion efficiency further. Panchromatic light absorption using a single near infra-red (NIR) dyes have been although attempted, however, TiO_2 based DSSCs show energetic matching limitations in terms of the electron injection and dye regeneration ultimately led to poor performance [3]. In order to circumvent this problem of single dye for panchromatic photon harvesting, use of multiple dyes either as dye-cocktail or positioning of dyes in dye bilayer approach have shown some success for efficiency enhancement in the recent past. In spite of some success using these approaches, constraints like inter-dye unfavorable interactions and complexity involved in selective positioning of dyes in bilayer architecture are still existing hurdles [4-5].

Another possible approach towards utilization of multiple dyes for panchromatic photon harvesting is the implementation of tandem device architecture. According to SQ limit the tandem approach evade the performance limitation established by single junction solar cells. The electrical and optical stacking of multiple DSSCs (tandem DSSCs) avoid the efficiency limitation imposed and can be realized either



in series or parallel interconnection. Series arrangement needed the respective top cell and bottom cell (sub cell) short circuit current density (J_{sc}) matching emanating in the enhanced open circuit voltage (V_{oc}). Mechanically stacked tandem DSSCs architecture possess numerous advantages due to ease of fabrication, independent control and optimization and top as well as bottom cells along with flexibility for selection and utilization of redox electrolytes. The first tandem DSSCs was explored and reported by He et al by utilizing n-p photoanodes [6]. Although realization of tandem DSSC was demonstrated by enhanced V_{oc} but overlapped spectra of corresponding sub cells resulted in to $< 1\%$ external power conversion efficiency (PCE). Owing its simplicity and huge possibility of combining different types of top and bottom cells such as DSSC/DSSC [7, 8], DSSC/Copper-indium-gallium selenide (CIGS) [9-10], DSSC/Silicon [11], DSSC/Perovskite [12] and DSSC/bulk heterojunction [13] etc., series connected mechanically stacked tandem solar cells have been most extensively investigated aiming towards enhancement in the overall PCE by enhancing the V_{oc} . In all these attempts, in spite of some success on the enhanced PCE due to V_{oc} enhancement, bottle-neck still lies in the control and optimization of optical losses by intermediate layers, glass, and top cell hindering the photon reaching to the bottom cell. Especially in the case of DSSC/DSSC tandem cells, superfluous intermediate TCO layer used in the stacked tandem DSSCs are liable for loss of the photon flux accessible to bottom cell. It is reported that about 20% photons are lost while transmitting from the top cell and intermediate layers [14-15].

Intermediate layers have been found to play a crucial role towards the realization efficient tandem solar cell and consequence of their presence have shown to affect the photovoltaic performance adversely not only in the perovskite-Si but also perovskite-CIGS tandem solar cells [16-17]. To deal with such unavoidable losses by intermediate layers, efforts have been directed to fabricate n-p tandem solar cells utilizing p-NiO as photocathode. Conceptually, the n-p tandem architecture seems to be better than conventional n-n tandem design, since it not only omits intermediate glass layers but also there is no need of expensive Pt counter electrode and simplicity of the tandem design. Contrary to n-DSSC, p-DSSC has not got much attentions owing to their very low reported efficiency ($< 0.2\%$) [18]. Even best p-DSSC developed so far, its implementation in n-p tandem DSSC has led to external PCE of $< 2\%$ [19]. Apart from this other approaches in terms of alteration and modification of intermediate layers by utilizing Pt-coated metal mesh have also been attempted in parallel tandem DSSC configuration. [20-21]. Enhanced J_{sc} has been although demonstrated but such architecture are only valid to DSSC/DSSC tandem solar cells limiting its wide spread hybridization with other kind solar cells. Till date best PCE has been demonstrated by mechanically stacked series connected tandem solar cells but in most commonly employed tandem architecture four TCO plates are being used. It not only offer additional cost burden since TCO is one of the costly components of DSSC [22] but also offers the optically loses for the incident photons to the bottom cell coming through the top cell. Removal of TCO layers as much as possible from the tandem DSSC architecture is expected to be one of the amicable solutions for such issues. We have shown that even after removal of costly TCO components, observed PCE is only slightly lower as compared to their TCO based DSSC counterparts in these cases of both of the Iodine as well as cobalt complex based redox electrolytes [23-24]. Utilization of TCO-less DSSC The utilization of TCO-less DSSCs as bottom electrode in tandem cell have also to enhance the photon harvesting ultimately promoting the PCE [25]. Present article deals with fabrication and characterization of mechanically stacked and series connected TCO-less tandem DSSCs in different device architectures aiming towards optimization of the intermediate layers and its implication on the photon harvesting with various complementary dye combinations.

2. Materials and Methods

The F-doped SnO_2 glass was purchased from OPV tech. All solvents were purchased and used without further processing. For catalytic action a very thin layer platinum (Pt) were coated on the TCO layer by CFS-4EP-LL, (Shibaura Mechatronics, Japan). Sensitizing dyes 2-Cyano-3-[4-[4-(2,2-diphenylethenyl)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopent[b]indol-7-yl]-2-propenoic acid (D131) and Di-tetrabutylammonium-cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719) were purchased from Mitsubishi Paper mills Ltd. and Solaronix, respectively. The electronic

absorption spectra of dyes used in the present work has been measured using UV-visible spectrophotometer (JASCO, V550). The photovoltaic characterization were measured with solar simulator (CEP-2000 Bunko Keiki BSO-X150LC) and the photocurrent action spectra were performed with constant photon flux of 1×10^{16} photons per cm^2 at each wavelength in DC mode. The IV performance were measured under AM1.5 condition with 100 mW/cm^2 solar irradiation by placing of 0.2025 cm^2 black metal mask.

TCO based as well as back contact TCO-less bottom cells were fabricated as per our earlier publication [15]. In order compare the performance of TCO-less tandem DSSC, conventional four TCO-based tandem DSSC were also fabricated. Device architecture of conventional TCO-based tandem DSSC is shown in the figure 1. Two types of conventional TCO-based tandem DSSC (T and T2) were fabricated depending on utilization of sensitizing dyes used in the top and bottom cells. T-tandem DSSC consists of visible photon harvesting sensitizing dyes D-131 and N-719 dyes in the top and bottom cells. The photoanode sensitized with 0.5 mM D131 (1:1 (v/v), acetonitrile: t-butyl alcohol) was assembled with 1 nm transparent Pt coated FTO glass and constitutes the top cell. Mesoporous TiO_2 layer of the bottom cell photoanode was constructed by $15\text{--}20 \text{ nm}$ particle size of semi-transparent D/SP paste and sensitized by 0.3 mM N719 (1:1 (v/v), acetonitrile: t-butyl alcohol) was assembled with 60 nm Pt sputtered FTO glass. The electrolyte utilized in top cell and bottom cell includes I_2 (50 mM), LiI (500 mM), 4-tert-butyl pyridine (580 mM) and 1-ethyl-3-methylimidazolium iodide (600 mM) in dehydrated acetonitrile. On the other hand T2-tandem DSSC was fabricated by utilizing visible light harvesting N-719 dye in the top cell while NIR photon harvesting dye PC-25 in the bottom cell. The top cell photoanode sensitized with N719 ($3 \mu\text{m}$) was assembled relatively thicker ($14 \mu\text{m}$) bottom cell photoanode. Mesoporous TiO_2 paste with larger particle size (D37) favouring the better dye absorption of bulky PC25 were employed in bottom cell photoanode. Electrolyte involved were Top cell: I_2 0.05 M , LiI 0.1 M , 4-tBuPy 0.5 M and 1,2DPII 0.6 M and bottom cell: I_2 0.05 M , LiI 1 M and 1,2DPII 0.6 M in dehydrated acetonitrile.

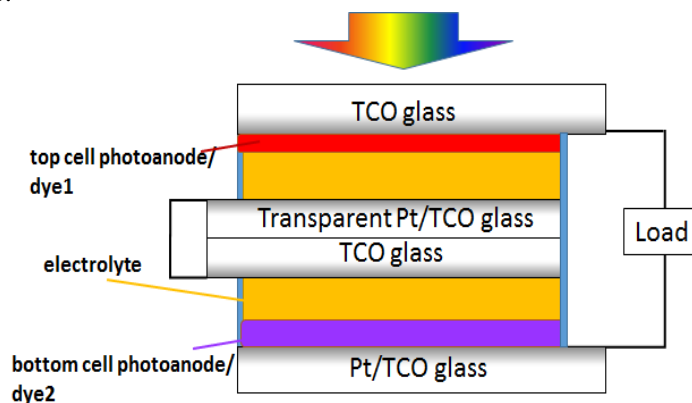


Figure 1. Mechanically stacked conventional tandem DSSCs (T/T2 tandem DSSCs) architecture showing superfluous intermediate TCO layers.

TCO-less tandem DSSCs were fabricated by replacing the TCO-based bottom cell of the tandem DSSC with the back contact TCO-less bottom cell. Device architectures adopted in the TCO-less tandem DSSC fabrication has been schematically shown in the figure 2. Two types of TCO-less tandem DSSCs (T1 and T3) which are analogous to their corresponding conventional TCO based tandem DSSC counterparts. TCO-less back contact DSSCs consisting of glass or plastic film/electrolyte-dye/ TiO_2 /protected SUS metal mesh/PTFE-spacer/Pt-FTO glass was fabricated as per our earlier publications [24]. The fabrication process basically involves the screen printing of mesoporous TiO_2 paste (D/SP) on protected SUS mesh followed by baking at 450°C for 30 minutes. Sensitizing dyes D131 and N719 were used in the top and bottom cells, respectively of the T1 TCO-less tandem DSSC. On the other hand, T3 TCO-less tandem DSSC includes dyes N719 and PC25 in the top and bottom

cells, respectively. Electrolyte composition for respective dyes were the same as used in the conventional tandem DSSCs (T and T2). It should be noted that TCO-less tandem DSSC (T1) utilizes three TCO layers while TCO-less tandem DSSC architecture T3 not only uses only two TCO layers but also the flexible and more transparent ITO/PET film as intermediate layer.

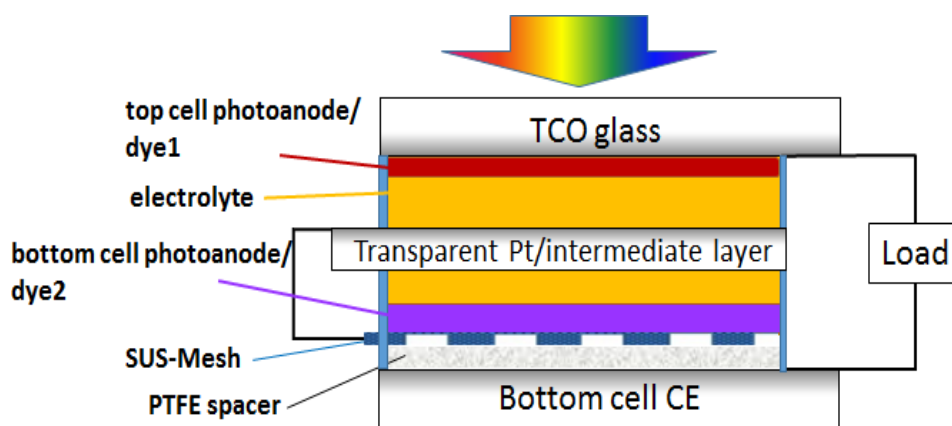


Figure 2. Mechanically stacked TCO-less tandem DSSCs architecture (a) T1 TCO-less tandem DSSCs: FTO/TiO₂/D131/Pt-FTO/N719/TiO₂/SUS-mesh/PTFE/Pt-FTO (b) T3 TCO-less tandem DSSCs: FTO/TiO₂/N719/Pt-ITO-PET/PC25/TiO₂/SUS-mesh/PTFE/Pt-Ti foil.

3. Results and Discussion:

Tandem DSSCs take the advantages of possibility for wide wavelength photon harvesting by the independent and judicious selection of sensitizing dyes having complementary electronic absorption. This offers the possibility of not only enhancing J_{sc} by wide wavelength photon harvesting but also enhancement in the V_{oc} by connecting the top and bottom cells in series. In the case of series connected tandem solar cells non-complimentary light absorption by top and bottom cells, although leads to enhanced V_{oc} but final out external PCE is either unchanged are slightly improved [26-27]. Taking these points in to consideration we have utilized sensitizing dyes D131, N719 and PC25 having complementary electron absorption spectra which has been shown in the figure 3 along with their molecular structure [15, 25].

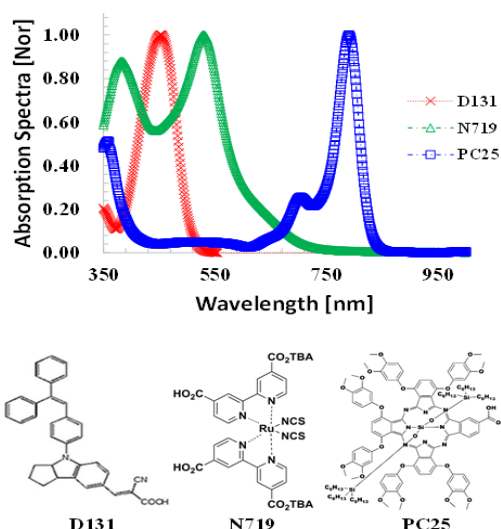


Figure 3. Solution-state electronic absorption spectra of sensitizing dyes D131, N719 and PC25 along with their molecular structure.

It can be clearly seen that dye D131 has a very strong light absorption between 350-550 nm regions where N719 exhibits diminished absorption. At the same time, PC25 exhibits intense light absorption in the NIR 750-900 nm where N719 is unable to absorb any light in this region. This justifies the selection of D131 with N719 or N719 with PC25 for the series connected mechanically stacked tandem DSSC fabrication. As a proof of concept and device functioning of mechanically stacked and series connected tandem DSSCs, a set of sensitizers (D131, N719) having complementary light absorption mainly in the visible region were taken in to consideration. First of all, a conventional tandem DSSCs using four TCO glasses with intermediate TCO layer (T tandem DSSCs) in device architecture as shown in the figure 1 was fabricated by mechanically stacking the top cell and bottom cell.

In this, incident photons have to travel through the dye-adsorbed mesoporous TiO_2 layer of top cell to the bottom cell. During this, photons of high energy are absorbed by the dye stained top cell and remaining un-utilized low energy photons are transmitted to the bottom cell via intermediate layer for the photon harvesting. Since best tandem performance can only be obtained by the proper matching of J_{sc} from top and bottom cell, it is necessary to control the thickness top cell photoanode and has been found to be of 1 μm in the case top cell using the D131 dye [15]. Photovoltaic performance of the various tandem DSSCs fabricated in this present work has been shown in the figure 4 along with their photovoltaic parameters shown in the table 1. Under optimized thickness of D131 sensitized top cell (1 μm) and N719 sensitized bottom cell (14 μm), this T tandem DSSC exhibits a short-circuit current density (J_{sc}) of 6.96 mA/cm^2 , open circuit voltage (V_{oc}) of 1.40 V and a fill factor (FF) of 0.65 leading to the external PCE of 6.96 % under simulated solar irradiation. In this T tandem DSSC, a perusal of photovoltaic parameters of individual top cell (PCE 3.53 %, J_{sc} 7.17 mA/cm^2 , FF 0.67, V_{oc} 0.73 V) and bottom cell (PCE 2.89 %, J_{sc} 6.07 mA/cm^2 , FF 0.71 V, V_{oc} 0.67 V) clearly corroborates not only the series connected tandem formation due to summation of top and bottom cell V_{oc} (1.40 V) but also the enhanced external PCE of 6.96 % due to complementary photon harvesting by the respective dyes.

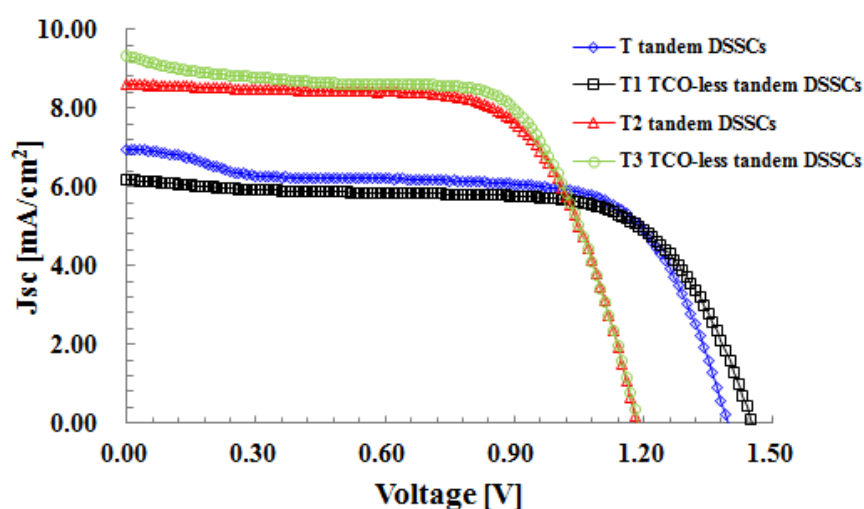


Figure 4. Photovoltaic characteristics of various type of tandem DSSCs after simulated solar irradiation fabricated for present investigation.

Conventionally fabricated T-DSSCs have mechanical rigidity owing to the presence of four TCO glasses which offers the handling and transportation purposes. Apart from this, intermediate TCO layers are not only liable towards reflection and transmission induced photon losses but also imposes addition cost burden. This indicates that suitable countermeasures are needed to adopt the tandem device architectures which are not only efficient in terms of optical management but also cost effective. Amongst available architectural approaches, utilization of TCO-less back contact DSSCs established themselves as one of the cost effective and optically efficient device architectures. Keeping these points

in mind, TCO-less tandem DSSC (T1 TCO-less DSSC) was fabricated by stacking a TCO-less DSSCs as bottom cell with the TCO-less top cell DSSCs in figure 2 (device a). Superiority of this fabricated T1 TCO-less tandem DSSCs lies in its economical architecture in which one of the four TCO layers from T tandem DSSC (figure 2a) was removed. This T1 TCO-less tandem DSSCs bearing economical architecture also offers advantageous impact in terms improved light transmission from top cell and intermediate TCO layers reaching to bottom cell is shown in the figure 5. It clearly demonstrates the preference and optical advantage available at bottom cell photoanode by added up 20% photons with respect to conventional T tandem DSSCs [25].

Table 1. Photovoltaic parameters for various tandem-DSSC fabricated in the present work.

Type of tandem DSSCs	PCE (%)	FF	V _{oc} (V)	J _{sc} (mA/cm ²)
T Tandem	6.28	0.65	1.40	6.96
T1 TCO-less	6.06	0.68	1.45	6.17
T2 Tandem	6.88	0.68	1.18	8.61
T3 TCO-less	7.19	0.65	1.19	9.34

In order to attain the maximum photovoltaic performance by this T1 TCO-less tandem DSSCs, it is necessary to optimize the performances of top and bottom sub cells especially to match the output Jsc promoting the enhanced FF. Optimization of thickness and dye combinations in top and bottom cells aiming to towards enhancing the PCE of conventional tandem DSSCs have also been systematically performed by Yamaguchi et al [8]. In this work authors clearly demonstrated that mismatch of Jsc of top and bottom cells leads to highly hampered PCE especially due to poor FF. In this work, performances of individual top and bottom cells were first optimized for comparable Jsc which were found to be Jsc 6.12 mA/cm², Voc 0.76 V, FF 0.66, PCE 3.06 %) and Jsc 5.79 mA/cm², Voc 0.68 V, FF 0.72, efficiency 2.83 % for TCO based top cell and TCO-less bottom cells, respectively. Mechanical stacking and series connection of these optimized top and bottom cells, this T1 TCO-less tandem DSSC, exhibits a Jsc of 6.17 mA/cm², Voc of 1.45 V and FF of 0.68, leading to external PCE of 6.06 % under simulated solar irradiation (figure 4 and table 1). This clearly indicates that even after removal of one of TCO layer from the conventional tandem DSSC using four TCO layers final external PCE is not being much affected.

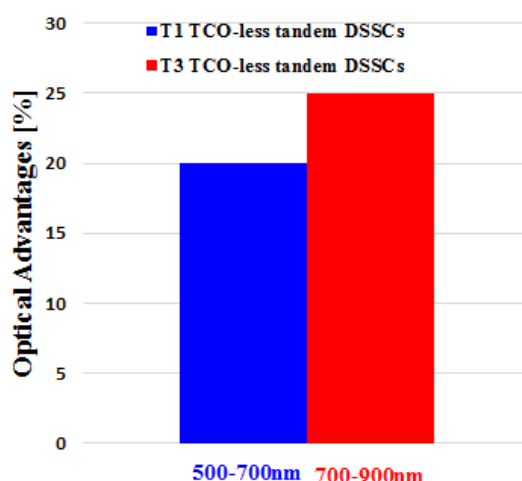


Figure 5. Optical advantages associated with (a) T1 TCO-less tandem DSSCs (b) T3 TCO-less tandem DSSCs with respect to respective dye stained conventional T/T2 tandem DSSCs.

Solar spectrum is consisted of photons encompassing from the ultraviolet to far IR wavelength region, therefore a panchromatic photon harvesting in wide wavelength region is inevitable for the enhanced

photovoltaic performance of the solar cells. After verification of functioning and tandem formation using visible photon harvesting D131 and N719, efforts have been directed to attain panchromatic photon harvesting by judicious selection of dyes having complementary light absorption. To achieve this goal, series connected and mechanically stacked conventional tandem DSSC (T2 tandem DSSC, figure 1) was fabricated using visible photon harvesting N719 dye in the top cell while complementary NIR light absorbing Si-Phthalocyanine dye (PC25) in the bottom cells. First of all optimization of top cell and bottom cell photoanode thicknesses along with electrolyte composition were conducted in order match the maximum possible J_{sc} as per our earlier publication before the T2 tandem DSSC fabrication [25]. The photovoltaic performances for optimized top and bottom cells were found to be J_{sc} 8.40 mA/cm², V_{oc} 0.40 V, FF 0.61, PCE 2.06 % (bottom cell) and J_{sc} 8.72 mA/cm², V_{oc} 0.78 V, FF 0.70, PCE 4.77 % (top cell) after simulated solar irradiation. Thus it can be seen that wide photon harvesting due to utilization of visible and NIR dyes has led to the possibility of matching the higher J_{sc} . Mechanically stacked series connected T2 tandem DSSC fabricated using these optimized TCO based top and bottom cell led to attain a J_{sc} of 8.61 mA/cm², V_{oc} of 1.18 V, FF of 0.68, resulting in to external PCE of 6.88% (figure 4 and table 1) which is higher as compared to its T tandem DSSC counterpart.

Wearable and flexible DSSCs have shown the prominence in utilization of plastic based TCO layers. ITO-PET film exhibits light weight is suitable for the large scale roll to roll fabrication of printed photovoltaic devices. At the same time, Titanium (Ti) foil is has been emerged as cost-effective and flexible alternative to TCO glass along with higher electrical conductivity [28]. Keeping these points in to consideration, further refinement in the T1 TCO-less tandem DSSCs architecture has been carried out in terms of proposal of T3 TCO-less tandem DSSCs as shown in the figure 2 (b). In this T3 TCO-less tandem DSSC, not only flexible intermediate ITO-PET has been used but also flexible Pt-coated Ti-foil has been used as the counter electrode of the TCO-less bottom cell. Utilization of this ultrathin Pt-coated ITO-PET as intermediate layer not only offers the possibility towards the realization of flexible DSSC but also it offers the optical transmission advantage where about 25% more photons are available at the bottom cell photoanode as shown in the figure 5. Top and bottom cell dyes, optimized thicknesses and electrolyte compositions were the same as used in the conventional T2 tandem DSSC. The photovoltaic performances shown by respective sub cells were found to be J_{sc} 8.13 mA/cm², V_{oc} 0.40 V, FF 0.62, PCE 2.04 % and J_{sc} 9.65 mA/cm², V_{oc} 0.75 V, FF 0.67, PCE 4.82 % for the bottom and top cells, respectively. Under simulated solar irradiation this T3 TCO-less tandem DSSC exhibits a photovoltaic performance of 7.19 % (J_{sc} 9.34 mA/cm², V_{oc} 1.19 V, FF 0.65) which is higher than its conventional T2 tandem DSSC counterpart (figure 4 table 1). Therefore, by judicious selection of device architecture and dye combinations and top and bottom cells, it is not only possible to remove two costly TCO components but also the enhanced PCE for the T3 TCO-less tandem DSSCs.

4. Conclusions

In summary, we have successfully demonstrated the fabrication and characterization of light efficient and cost-effective TCO-less tandem DSSCs utilizing visible wavelength region photon harvesting sensitizing dyes D131 and N719. Further modification in the TCO-less tandem architecture was succeeded with fabrication of flexible TCO-less bottom cell and optically more transparent ITO-PET employing Pt-coated Ti foil as counter electrode and intermediate layer, respectively. Introduction of panchromatic photon harvesting by utilizing visible dye N719 in top cell and Si-phthalocyanine dye PC25 in bottom cell and their implementation to fabricate the T3 tandem TCO-less DSSC led to the best external power conversion efficiency of 7.19 % under simulated solar irradiation. In spite of the removal of two costly TCO components out of four in conventional series connected tandem DSSC, there was no any adverse effect on the observed external PCE. Efforts are still needed to design and develop novel NIR dyes with relatively higher V_{oc} in order to attain further enhancement in the PCE.

Acknowledgments

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