

Controlling the TiO₂-Dye Nanomolecular Interactions for Improving the Photoconversion in Transparent Dye-sensitized Solar Cells

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Abstract

Transparent dye-sensitized solar cells (DSSCs) have been fabricated using two sensitizing dyes aiming towards panchromatic photon harvesting following two different approaches of dye adsorption such as using dye-cocktail and sequential dye adsorption. A combination of complementary yellow-coloured dye (D-131) and green-coloured far-red-sensitive squaraine dye (SQ-140) was judiciously selected not only for panchromatic light absorption but also for bypassing the absorption in the high eye-sensitivity wavelength region (500-600 nm) region to improve the transparency. The DSSC fabricated using a dye cocktail of D-131 and SQ-140 in a 9:1 molar ratio exhibited a photoconversion efficiency (PCE) and average visible transparency (AVT) of 3.89 % and 36.9 %, respectively. On the other hand, stepwise and controlled dye adsorption of SQ-140 followed by D-131 on mesoporous TiO₂ led to further improvement in the PCE from 3.89 % to 4.50 %, while AVT was reduced from 36.9 % to 15.6 %. This marked improvement in the PCE for the stepwise co-sensitized transparent DSSCs was attributed to the suppression of unfavourable inter-dye interaction leading to synergistic photon harvesting by both of the constituent sensitizing dyes.

1. Introduction

In the present world to maintain a good quality of life there is a need for a huge amount of energy leading to the global energy crisis. By consuming fossil fuels such as coal, gas and petroleum, the emission of greenhouse gas has crossed the tolerance limit and as a result, we are getting polluted and facing global warming issues as well. Depleting fossil fuels is also a serious issue for future generations to live in this world by maintaining the present quality of life. Therefore, the research focus has been directed to develop sustainable and eco-friendly energy harvesting from renewable energy resources. Among all the non-conventional energy resources, solar energy has become a reliable source, and at the same time, it is sustainable too. Only Sun can give a huge amount of energy per day to the Earth, which is more than our need. By utilizing the photovoltaic effect, solar cells can directly convert light energy into directly usable electricity. Conventional silicon-based solar cells have already been commercialized to fulfill our energy demand but their fraction is still low.^[1] As the fabrication and installation of these silicon solar cells are highly expensive, research on the development of low-cost solar cells has got more attention in the recent past. Dye-sensitized solar cells (DSSCs) have been widely investigated because of their low raw material cost, beautiful colours and their potentiality for relatively high energy conversion efficiency with simple device architecture compared to conventional silicon solar cells.^[2] Moreover, in DSSC, as both anode and cathode are prepared by using transparent glass material, it has a great opportunity to participate in the power window applications for harvesting solar energy^[3, 4] while keeping the esthetic beauty.

In solar cells, the transparency of the device and power conversion efficiency are inversely proportional since an optimal thickness of the active layer is necessary for sufficient photon harvesting. On the other hand, an increase in the thickness of the active layer needed for enhanced light absorption leads to a decrease in the transparency of the solar cells. Though this is true for the non-wavelength selective photovoltaic systems, the case might be different for the DSSCs having the flexibility of the selection for the colour of the sensitizing dyes.^[5, 6] This has also been recently demonstrated by us that the colour of sensitizing dyes selected for fabricating transparent DSSCs has a strong influence on the thickness and transparency.^[7] For the commercial implementation of see-through/transparent solar cells targeted figures of merits such as efficiency, stability, flexibility and transparency of 10 %, 1500 hours, bending radius of 6 mm and 70 % must be cleared. In this context, Kang et al. reported transparent silicon-based solar cells by incorporating slits and holes with a PCE of 5% and 7% with a transparency of 60 % and 45 %, respectively.^[8] Very high transparency between 65-75 % has been reported

for organic thin films solar cells, DSSCs and perovskite solar cells with PCE of 1.5-2.0 %, 2.9 % and 1.6 %, respectively. ^[9-11] The high transparency of reported organic thin film solar cells and DSSCs has been attributed to the utilization of NIR-sensitive p-type semiconductor and NIR cyanine dye, respectively, which do not absorb light in the high eye-sensitivity wavelength region of 500-600 nm. This opens the door for designing novel functional materials to unlock the bottleneck of the PCE-transparency barrier.

The functioning of the DSSC is based on mimicking natural photosynthesis and utilizes the basic electrochemical process to generate electricity by absorbing photons. Photon is absorbed by a monolayer of sensitizer and adsorbed on mesoporous semiconductor nanoparticles (Titanium dioxide). Therefore, sensitizing dye plays a vital role in power conversion and controlling the power conversion efficiency (PCE) of DSSCs. To enhance photon harvesting, a panchromatic light absorption encompassing from visible to infrared (IR) wavelength region and their efficient conversion into electricity is inevitable. In general, organic dyes have a narrow optical absorption window owing to their excitonic nature. The basic idea is to utilize multiple dyes simultaneously, which can be easily implemented in DSSCs. ^[12] Making a dye cocktail by mixing two or more sensitizing dyes with complementary optical absorption in different molar ratios is a fantastic approach towards fabricating a panchromatic DSSC. ^[13, 14] In this dye-cocktail system is expected to get increased PCE as compared to single dye-based DSSCs. Whereas, in practice, it is very common to happen competitive adsorption of dyes onto TiO₂ surface as the rate of dye adsorption and the binding strength of dye with TiO₂ varies depending on the nature of the dyes under consideration. ^[15] As a consequence, due to the lack of optimal dye loading and differential photon harvesting the cell performance may not be synergistic. ^[16] Therefore, many research works have been conducted to separate the dye molecules upon the TiO₂ surface to overcome this issue. ^[17, 18] For the separation of dye molecules utilizing a metal oxide layer in between sensitizing dyes requires many special conditions to maintain, which makes it inconvenient for large-scale production of DSSCs. At the same time, stepwise co-sensitization is a very simple method to enhance PCE in the case of multiple dye-based DSSCs. This method relies on studying the adsorption behavior of dyes onto the mesoporous semiconductor layer enabling to decide the sequence of dye adsorption. This helps to ensure optimal dye adsorption by suppressing the unfavourable inter-dye interaction and hence increasing the overall PCE of the DSSCs.

In this present research, this stepwise dye adsorption method has been conducted parallel with the dye-cocktail adsorption system to investigate their implication on the differential

photovoltaic performance of transparent DSSCs thus fabricated. For making DSSCs transparent for their suitability for application in building integrated photovoltaics (BIPV), the dye should be selected judiciously to avoid high eye-sensitivity (500-600nm) wavelength region.^[19] Therefore, this work has been done utilizing two dyes with optical absorption beyond the high eye-sensitive region. To accomplish this, a D-131 dye, which is commercially available and novel far-red-sensitive unsymmetrical squaraine dye SQ-140 synthesized in our laboratory were utilized for the fabrication and characterization of transparent DSSCs. The molecular structure of the sensitizing dyes is shown in **Figure 1**. Transparent DSSCs have been fabricated using dye cocktails in different molar ratios and their stepwise or sequential adsorption to investigate their implications on the PCE and transparency of DSSCs in detail.

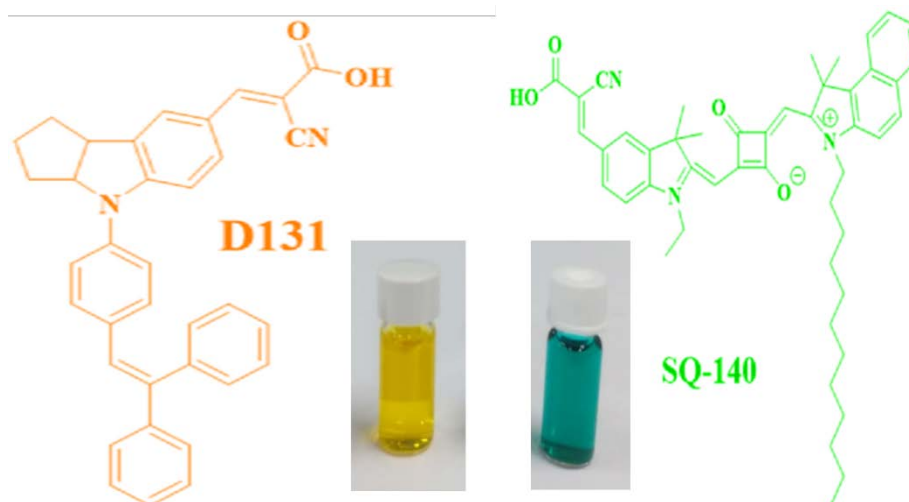


Figure 1. Chemical structure of the dyes D-131 and SQ-140 and photographs of the dye corresponding dye solutions in ethanol

2. Experimental

Solvents like acetone, isopropanol, ethanol, acetonitrile and t-butanol were used for washing the electrodes and making dye solutions were procured from Wako chemical company, Japan and used as supplied without any further purification. Fluorine-doped tin oxide (FTO) glass was used for the fabrication of the working photoanode and counter electrodes. FTO glass was purchased from Asahi glass company Japan having a sheet resistance of 18 Ω /sq. For preparing electrodes, the FTO glass substrates were cleaned ultrasonically by detergent, distilled water, acetone, and isopropanol successively for 10 min each followed by UV-Ozone treatment (UV-O₃ cleaner, Laser Techno, Japan) for 10 min. For the working electrode, TiCl₄ surface treatment has done by dipping the substrates in 40 mM aqueous TiCl₄ solution at 70 °C for 1 h. After rinsing with water and ethanol, it was sintered at 450 °C for 30 min. Transparent titanium oxide

paste (TiO₂) (Ti-Nanoxide, T/SP) was purchased from Solaronix, SA, Switzerland and screen printed on the FTO surface to coat the transparent mesoporous TiO₂ layer using metal mesh. The screen-printed thin TiO₂ film was sintered in a temperature-programmable muffle furnace (FO100, Yamato, Japan) at 500 °C for 1 h. After backing the TiO₂ layer, a surface profiler (SURFCOM 130A, Accretch, Japan) was used to determine the thickness of the film. This coating and sintering process was repeated to get the thickness of transparent TiO₂ film to be about 10 μm. TiO₂-coated FTO glass substrates were dipped in the respective dye solution for dye adsorption. The Indolene dye (D-131) was purchased from Mitsubishi paper mills limited, Japan, whereas green-coloured unsymmetrical squaraine dye (SQ-140) was synthesized as per our earlier published work.^[20] The chemical structure of the sensitizing dyes is shown in Fig 1. Two types of sensitizing dyes, i.e., D-131 (0.5 mM) and SQ-140 (0.2 mM) were used in this study. For making the dye solution a mixture of acetonitrile and t-butanol was used as the solvent for D-131 dye while it was ethanol for SQ-140. To prevent dye aggregation 20 mM of chenodeoxycholic acid (CDCA) was added with squaraine dyes as co-adsorber and prevent dye aggregation was purchased from Wako pure chemical industries, Japan.

For transparent DSSCs using a single dye-sensitizer, optimized dye adsorption time of 4 hours and 5 hours for the dyes SQ-140 and D-131, respectively. In the case of fabrication of transparent DSSCs using stepwise dye adsorption of SQ-140 and D-131, the same dye solution used for single dye-based DSSCs was used. To fabricate the photoanode of transparent DSSCs under stepwise dye adsorption, 10 μm thick transparent TiO₂ was first dipped in 0.2 mM SQ-140 dye solution overnight for complete dye adsorption. After complete adsorption, photoanodes were rinsed with solvent and then dipped in 0.5 mM D-131 dye solution for different time intervals. At different time intervals of adsorption by D-131 dye, respective dye-adsorbed substrates were taken out, thoroughly washed with solvent and utilized as photoanodes for fabricating transparent DSSCs followed by photovoltaic characterizations. To fabricate transparent DSSCs using a dye cocktail of D-131 and SQ-140, different molar ratios of the respective dyes were taken using ethanol solvent and dye adsorption was carried out for 4 hours.

For making the counter electrode, Pt solution prepared from 2 mM solution of H₂PtCl₆ in isopropanol was spin-coated on FTO glass, which was sintered at 500 °C for 1 h in a muffle furnace. Iodine-based redox electrolyte consisted of Iodine (50 mM), lithium iodide (100 mM), t-Butylpyridine (0.5 M) and 1,2-dimethyl-3- propyl-imidazolium iodide (0.6 M) in acetonitrile

was filled in between the working and counter electrode to complete the DSSC. ^[7] For assembling the cells, a 25 μm thick hot melt spacer (Meltonix 1170-25) was purchased from Solaronix and at the end for sealing properly, UV curable resin (TB3017B, ThreeBond, Japan) was used. For the measurement of absorption spectra in solution as well as in solid-state for thin films adsorbed on transparent TiO_2 , a UV/visible-NIR spectrophotometer (JASCO V-570) was used. For the solid-state absorption spectral measurement dyes were adsorbed on the thin transparent TiO_2 (T/SP, Solaronix, 4 μm) coated on normal and cleaned glass substrates. Measurement of the photovoltaic performance of DSSCs was carried out using a solar simulator (CEP-2000 Bunko Keiki Co. Ltd, Japan) equipped with a Xenon lamp (Bunko Keiki BSO-150LC) used as a source of simulated solar irradiation at 100 mW/cm^2 . The power of the light exposure was calibrated using an amorphous Si photodetector (Bunko Keiki BS-520S/N 353). Photocurrent action spectra were also measured with a constant photon flux of 1×10^{16} $\text{photon}/\text{cm}^2$ in DC mode using the action spectrum measurement system connected to the solar simulator. The device area during the photovoltaic measurement was fixed to be 0.25 cm^2 using a black metal mask.

3. Results and discussion

3.1. Electronic absorption spectra

Electronic absorption spectra of dyes in ethanol solution and in solid-state (dyes adsorbed on TiO_2 layer) were measured using a UV-visible spectrophotometer and are shown in **Figure 2**.

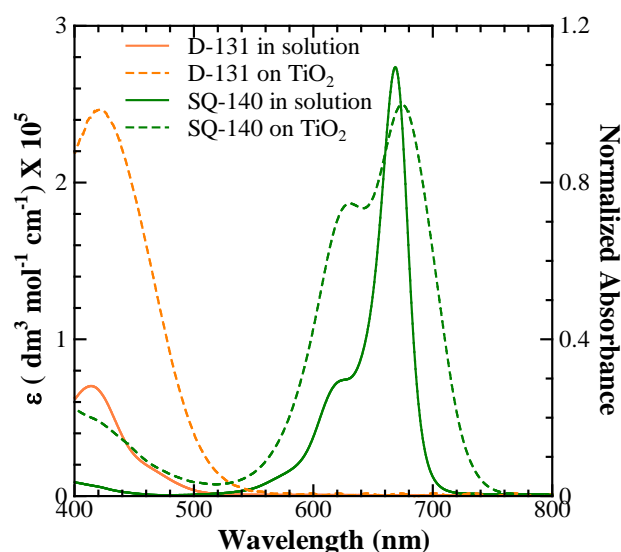


Figure 2. Electronic absorption spectra of sensitizing dyes D-131 and SQ-140 (5 μM) in acetonitrile /*t*-butanol and ethanol, respectively. In the case of SQ-140 a 100 times CDCA was also used as a dye coadsorber for preventing dye aggregation. The dotted line represents

corresponding normalized solid-state absorption spectra for dyes adsorbed on the 5 μm thick transparent TiO_2 .

It can be seen from this figure that dyes under investigation not only show the complementary optical absorption from visible to NIR wavelength region but also avoid the light absorption in the high eye-sensitivity wavelength region of 500 nm-600 nm ensuring their suitability for fabrication of the transparent DSSCs. From the Fig. 2, it is clearly shown that the absorption maximum (λ_{max}) of D-131 dye in acetonitrile and tert-butyl alcohol (1:1) solution is found at 414 nm, whereas for green-coloured unsymmetrical squaraine dye SQ-140 in ethanol solution it appears at 668 nm. As a D- π -A system, λ_{max} for D-131 dye arises from the intramolecular charge transition (ICT) having a molar extinction coefficient (ϵ) of $7.02 \times 10^4 \text{ dm}^3/\text{mol cm}$. On the other hand, SQ-140 dye has an order of magnitude higher ϵ of $2.73 \times 10^5 \text{ dm}^3/\text{mol cm}$, which is associated with the π - π^* transition from HOMO to LUMO of the dye. Due to the extended π -conjugation in the chemical structure, planarity promotes the delocalized intramolecular charge transfer from the HOMO to the LUMO, which is responsible for the high value of ϵ .^[21]

In the case of solid-state electronic absorption of dyes after their adsorption on the TiO_2 surface, dyes exhibit red-shifted λ_{max} along with little spectral broadening due to the interaction of dye molecules with the TiO_2 surface. The noticeable shoulder peak around 550-650 nm, which is a typical property of squaraine dyes associated with molecular aggregation shifted towards a lower wavelength than the monomeric absorption peak that appeared in solution, get more pronounced in the solid-state absorption spectra for the dye adsorbed on TiO_2 .^[22] Dye aggregation in the case of planer donor- π -acceptor (D- π -A) dyes has been widely reported to hamper the performance of DSSCs and the addition of CDCA with the dye solution has been widely used to suppress the dye aggregation and enhance the photon harvesting and photovoltaic performance of DSSCs.^[23, 24]

3.1. Photovoltaic characterization of transparent DSSCs

The dye sensitizer plays a pivotal role in enhancing the efficiency of a DSSC by absorbing light, whereas light transmission in the eye-sensitive region (500-600 nm) is a requirement to see across the DSSC. Therefore, aiming towards fabricating transparent DSSCs, sensitizers have been chosen in such a way that they absorb light bypassing the eye-sensitive region in solar spectra. In this work, we used dye D-131 absorbing in the visible wavelength region, whereas

SQ-140 dye absorbs the far-red region as shown in Figure 2. To increase the cell performance, utilizing multiple dyes is inevitable to attain wide wavelength photon harvesting. Two methods to utilize two or more dyes for fabricating DSSCs have been conducted in the present study. One is mixing dyes together in a common solvent (dye-cocktail) and another is dye to be adsorbed on a mesoporous TiO₂ layer by sequence (sequential/stepwise dye adsorption). As we know that the TiO₂ layer behaves as a scaffold for dye molecules in DSSC, a thicker layer is necessary for increasing current generation.^[25, 26] It has been reported in our previous work that a 10 μm thick TiO₂ layer is the optimum value for better performance (efficiency and transparency) of devices and in this work, the same thickness of the TiO₂ was utilized.^[7]

3.2.1. DSSC performance using dye-cocktail

Before preparing dye-cocktail-based DSSCs, single dye-based DSSCs were fabricated and characterized. Photovoltaic characteristics and photocurrent action spectra of transparent DSSCs fabricated using the constituent single dye sensitizer and two sensitizers from their dye cocktails prepared in different molar ratios are shown in **Figure 3** along with the summarization of photovoltaic parameters such as short-circuit density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and photoconversion efficiency (PCE) in **Table 1**. A perusal of this figure and table reveals that while decreasing the fraction of SQ-140 in the cocktail, the PCE was increasing gradually. The best photovoltaic performance of transparent DSSC was observed in the case of dye-cocktail consisting of D-131 and SQ-140 in a 9:1 molar ratio giving a J_{sc}, V_{oc} and FF of 8.99 mA/cm², 0.670 V and 0.646, respectively, leading to PCE a 3.89 %, which is higher than DSSCs based on single dyes and dye cocktails with other molar ratios of the two dyes. This observed result is attributed to the fact that the dye having a higher molar extinction coefficient (ϵ) is capable of imparting a significant role in enhancing the efficiency of hybrid DSSCs even with its presence in small amounts. It is clear from Figure 2 that the squaraine dye SQ-140 has 4 times higher ϵ than the D-131 dye, 9:1 molar ratio of those dyes giving higher efficiency. The photocurrent action spectrum, which is a basic plot of the incident photon to current conversion efficiency (IPCE) as a function of wavelength under monochromatic light irradiation was also recorded for transparent DSSCs using single dye sensitizers D-131 and SQ-140 along with that using dye cocktail giving the best performance (9:1) and are shown in **Figure 3(b)**. The action was taken not only to verify the result of increased J_{sc} for the dye-cocktail-based transparent DSSCs as compared to its single-dye counterparts but also to justify and probe the presence and extent of photon harvesting by the respective dyes in the dye cocktail.

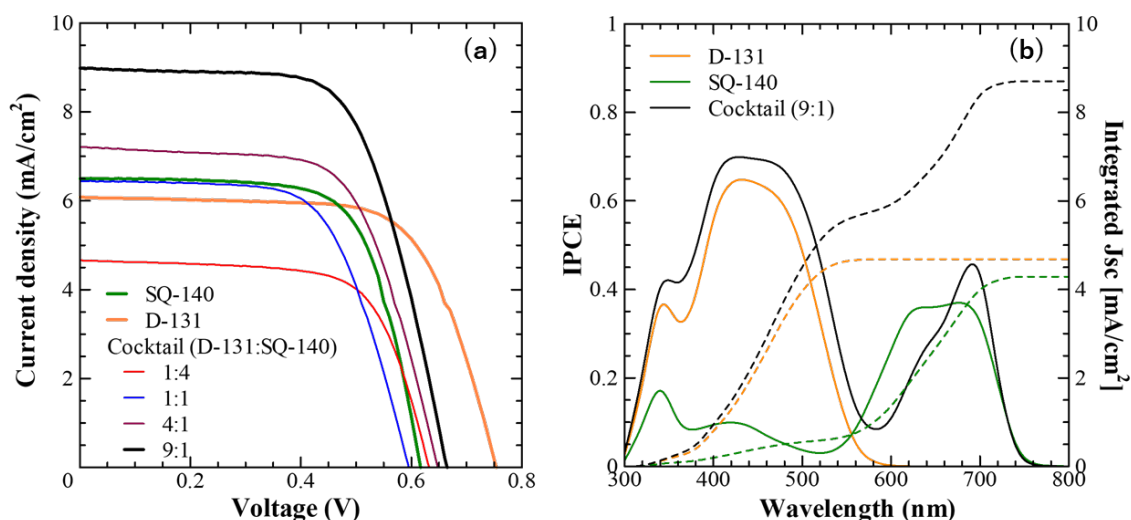


Figure 3. Photovoltaic characteristics (a) after simulated solar irradiation and photocurrent action spectra and integrated Jsc (b) after monochromatic light irradiation for the transparent DSSCs respective constituent dyes and their dye cocktails with different molar ratios.

Table 1. Photovoltaic parameters for transparent DSSCs utilizing dye cocktails of D-131 and SQ-140 dyes prepared in different molar ratios.

Molar ratio (D-131 : SQ-140)	Voc (V)	Jsc (mA/cm ²)	FF	PCE (%)
0:1	0.620	6.50	0.686	2.77
1:0	0.760	6.09	0.677	3.13
1:4	0.640	4.66	0.673	2.01
1:1	0.600	6.44	0.639	2.47
4:1	0.650	7.21	0.648	3.04
9:1	0.670	8.99	0.646	3.89

A perusal of Fig. 3(b) clearly corroborates that transparent DSSCs fabricated using dye cocktail exhibited photon harvesting by both in the 300-500 nm and far-red wavelength region of 600-750 nm associated with photon harvesting by both of the constituent sensitizing dyes D-131 and SQ-140 respectively, which is responsible for the observed enhancement in Jsc for dye-cocktail based DSSCs as shown in **Figure 3(a)**. It is worth mentioning here that the peak IPCE in the case of dye-cocktail were found to be enhanced as compared to their corresponding single dye-based DSSC counterparts, which might be attributed to the further mutual control dye aggregation leading to promoted charge injection. In an interesting report, Khazraji et al. have also emphasized that as compared to the dye aggregates, monomeric dye molecules are able to inject electrons into the conduction band of TiO₂ more efficiently. ^[27] A similar

synergistic photon harvesting by both of the constituent dyes of the dye cocktail using complex electrolyte based DSSCs by our group previously also.^[14] Although there was an enhancement in the PCE for the 9:1 dye cocktail as compared to single sensitizer-based DSSC, it might not be optimal owing to the possibility of unfavourable inter-dye interactions in the dye-cocktail system. On the other hand, the dye has its own nature of getting adsorbed on the TiO₂ layer, some are faster and some are slower. Moreover, there are differences in the binding strength of dye molecules with TiO₂.^[20] Therefore, the dye loading amount on the semiconductor surface might also be different. The non-synergistic PCE in this dye-cocktail method can be attributed to the presence of inappropriate fractions of the dyes on the TiO₂ surface as a result of inter-dye interaction due to the differential dye-loading.

3.2.2. DSSC performance using sequential dye adsorption

In a dye-cocktail system, a mixture of multiple dyes experiences inter-dye interaction, which hampers the PCE of the DSSCs. On the other hand, the interaction between dye molecules with the TiO₂ layer is also a key point to enhance efficiency, which is different for different dye molecules depending on their molecular structure. As dye absorbs photons for harvesting energy, getting the optimal amount of dye molecules attached to the TiO₂ surface is a necessary requirement to achieve high performance of DSSCs. Therefore, it is most necessary to attach the dyes separately to avoid undesirable interactions between dyes in the case of multi-dye-based DSSCs. A simple and excellent process has been realized to enhance photon harvesting and device performance by adsorbing the dye to the TiO₂ layer in a stepwise process, which allows the light to be captured at a wide range of wavelengths.^[28] In this work, stepwise dye adsorption has been conducted by utilizing two sensitizers (D-131 and SQ-140). In stepwise or sequential dye adsorption, the dye should be adsorbed on the TiO₂ surface one by one. In this study, as the primary sensitizer green-coloured SQ-140 dye was used, whereas D-131 dye was used as the secondary sensitizer. It is known that; dye loading time also plays an important role in adsorbing sufficient and effective amounts of dye molecules to enhance the PCE of DSSCs.^[7] Moreover, dye loading time is also responsible owing to the replacement of the weakly bound dye on TiO₂ nanoparticle by another having strong binding strength.^[29] Therefore, after complete adsorption of the primary sensitizer (SQ-140) on the TiO₂ layer, it was dipped in the solution of the secondary sensitizer (D-131) for different time intervals to optimize the condition for sequential dye adsorption giving the best PCE. Photoanodes thus prepared were used for the fabrication of transparent DSCCs and their photovoltaic characteristics after

simulated 1 Sun irradiation are shown in **Figure 4** along with the summarization of deduced photovoltaic parameters in **Table 2**.

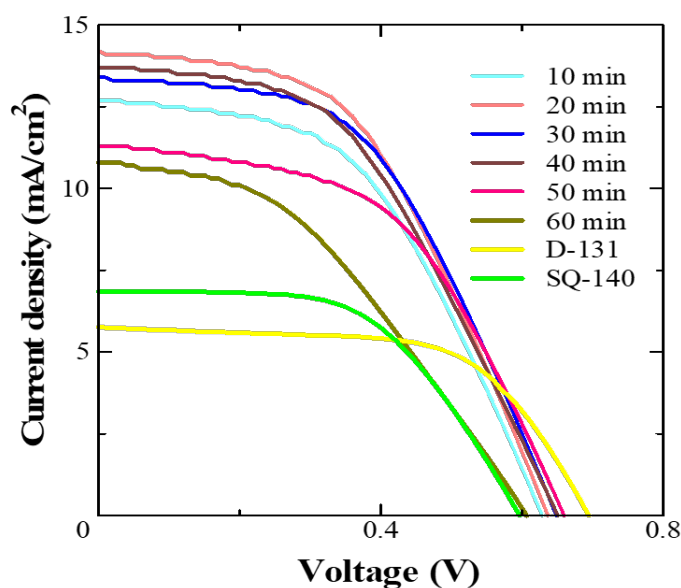


Figure 4. Photovoltaic characteristics for the transparent DSSCs fabricated by sequential dye adsorption of SQ-140 followed by D-131.

Table 2. Photovoltaic parameters for the transparent DSSCs fabricated by sequential dye adsorption of SQ-140 followed by D-131.

Dipping time in D-131	Voc (V)	Jsc (mA/cm ²)	FF	PCE (%)
10 min	0.63	12.68	0.49	3.94
20 min	0.64	14.15	0.50	4.53
30 min	0.65	13.36	0.50	4.36
40 min	0.65	13.73	0.47	4.19
50 min	0.65	11.34	0.51	3.81
60 min	0.61	10.82	0.41	2.66
D-131	0.70	5.77	0.62	2.48
SQ-140	0.60	6.85	0.56	2.30

It can be seen from Table 2 that transparent DSSCs fabricated using single D-131 and SQ-140 as sensitizers imparted a PCE of 2.48 % and 2.30 %, respectively. A small value of observed PCE in the transparent DSSCs thus fabricated is attributed to the constraints like the use of a relatively thinner TiO₂ layer (10 μm) for maintaining the transparency along with a

smaller optical absorption window of used sensitizers D-131 (350-500 nm) and SQ-140 (550-750 nm). After complete adsorption of SQ-140 on the TiO₂ layer, it was dipped in dye D-131 for 10 min, 20 min, 30 min, 40 min, 50 min and 60 min. From Table 2, we can see that DSSC utilizing co-sensitized photoanode dipped for 20 min in D-131 dye has given the best PCE of 4.53% by generating 14.15 mA/cm² J_{SC}, which is much higher as compared to that based on individual single dye-based solar cells. This could be considering the presence of an optimal amount of both dyes and their separation to avoid unfavourable inter-dye interactions leading to synergistic photon harvesting by both of the sensitizing dyes.

3.3. Average visible transparency of DSSCs

For a transparent DSSC, average visible transparency (AVT) is one of the important figures of merit to know the visibility across the device and its suitability for power window applications. To enhance the transparency across a coloured glass one of the amicable approaches is that it should pass the light of 500-600 nm wavelength, which falls in the high eye-sensitivity region. [19] In an interesting report, Zhang et al. demonstrated that there is a drastic fall in visual perception from 90 % to 10 % between the wavelength region of 500-600 nm. [14] This phenomenon is contradictory to fabricating the efficient DSSC since photon flux in the solar spectrum is highest in this wavelength region. Therefore, utilizing multiple dyes for wide-wavelength photon harvesting while bypassing the high eye-sensitivity region is an amicable method to fabricate DSSCs with high PCE in combination with high transparency. In this present work, D-131 dye and SQ-140 dye have been used as they harvest photons beyond the eye-sensitive region (Figure 2). The measurement of transparency takes into account transmittance (T), solar photon flux S at air mass 1.5 G and visual perception of the human eye (P), which can be represented by the following **Equation 1**. [30]

$$AVT = \frac{\int T(\lambda)P(\lambda)S(\lambda)d(\lambda)}{\int P(\lambda)S(\lambda)d(\lambda)} \quad (1)$$

It has been reported that the range of 25-38 % of AVT is a minimum acceptable value for BIPVs to see clearly. [31, 32]

AVT of a complete DSSC is affected by its various components such as TiO₂, Pt, dye molecules and electrolytes. Therefore, it is desirable to estimate the AVT for these components, which can be estimated by measuring the transmission spectra of these different components. At the same time, a perusal of the transmission spectra also reveals the relative presence and absence of both of the sensitizers in the photoanode prepared using two or more dyes by using

the dye cocktail or two dyes under stepwise dye adsorption. These considerations led to the measurement of transmission spectra of the complete DSSC, the corresponding photoanodes, and various components such as iodine-based redox electrolytes, TiO₂-coated FTO, and Pt-coated/FTO counter electrodes, which are shown in **Figure 5**. At the same time, AVT for each of them was also calculated using Equation 1, which is summarized in **Table 3**.

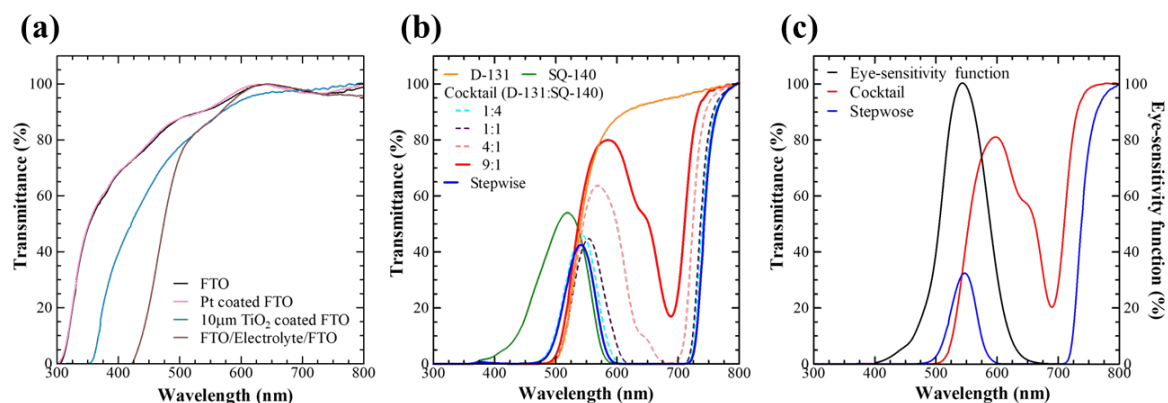


Figure 5. Transmission spectra of device components (a), photoanodes (b) and complete transparent DSSCs fabricated using optimum photoanodes along with the eye sensitivity function (c). Measurement of the transmission spectra was conducted with respect to air without using any reference substrate.

It can be clearly seen from Fig. 5(a) that transparent TiO₂ (T/SP) and Pt-coated FTO are highly transparent having the transmittance > 80 % after 500 nm. Iodine-based redox electrolyte is transparent in high eye-sensitivity regions and wavelength >500 nm but strongly absorb in 300-500 nm. A perusal of Fig. 3(b) and Table 3 reveals that AVT for the photoanode based on D-131 was higher (48.2 %) as compared to SQ-140 (31.1 %). This is attributed to the relatively higher absorption of light by SQ-140 in the 500-600 nm as compared to D-131 owing to its strong aggregation-assisted spectral broadening. The AVT for the photoanode with dye cocktail was found to increase from 26.0 % to 40.1 % as a function of increasing the molar ratio of D-131 in the dye cocktail, which was also reflected by transmission spectra shown in Fig. 3(b) indicating that decreasing fraction of SQ-140 in the dye cocktail leads to improved overall transmission in general and in the 500 nm to 600 nm in particular. Furthermore, the AVT of the photoanode prepared under stepwise optimized conditions was found to be 22.6 %, which is less than the AVT of the photoanode prepared by dye cocktail under the best condition of a 9:1 molar ratio. The AVTs of the complete DSSCs were estimated to be 36.9 % (Cocktail) and 15.6 % (Stepwise), respectively.

Table 3. Photovoltaic parameters for the transparent DSSCs fabricated by sequential dye adsorption of SQ-140 followed by D-131.

Transparent DSSC component	AVT (%)
FTO substrate	92.0
Transparent TiO ₂ layer / FTO	85.0
D-131 adsorbed on TiO ₂ / FTO	48.2
SQ-140 adsorbed on TiO ₂ / FTO	31.1
FTO/ Iodine-based electrolyte / FTO	94
Ultrathin Pt / FTO	100
Cocktail (D-131:SQ-140) /FTO	-
1:4	26.0
1:1	23.9
4:1	37.2
9:1	40.1
Stepwise / FTO	22.6
Complete DSSC dye cocktail	36.9
Complete DSSC stepwise	15.6

Two different methods, i.e., dye-cocktail system and sequential dye adsorption method have been utilized for the preparation of photoanodes and fabrication of transparent DSSCs using them, which are shown in **Figure 6**. In the dye-cocktail system, the 9:1 molar ratio of D-131 and SQ-140 has shown 36.9 % of AVT with a PCE of 3.89 %. On the other hand, DSSCs prepared by TiO₂ layer first adsorbed SQ-140 dye and then adsorbed D-131 for 20 min have shown 15.6 % of AVT with PCE of 4.5 %. A high AVT in the case of the dye cocktail system is the presence of a minimal amount of SQ-140 dye in the photoanode yielding light greenish-yellow colour to the DSSC. A perusal of Figure 2 also corroborates that D-131 dye only absorbs photons below 500 nm, which is completely out of the high eye-sensitivity region. On the other hand, the green-coloured dye SQ-140 absorbs some photons between 550-600 nm leading to slightly hampered AVT but enhanced PCE.

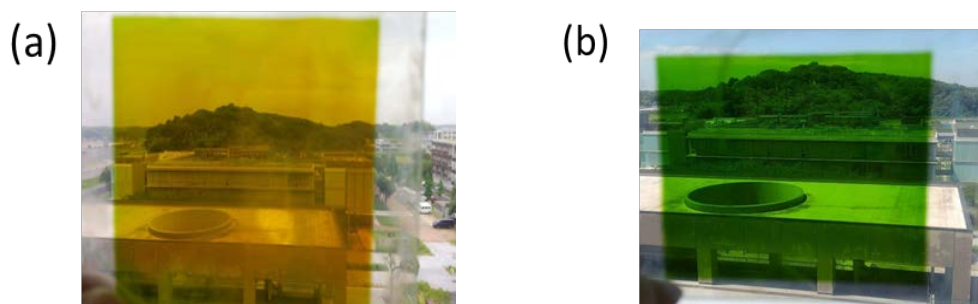


Figure 6. Photographs of photoanodes for transparent DSSCs under optimum conditions with a dye cocktail of D-131 and SQ-140 in a 9:1 molar ratio (a) and two-step sequential dye adsorption of SQ-140 (overnight followed by D-131 for 20 min (b)).

4. Conclusion

Transparent DSSCs have been fabricated by utilizing two dyes judiciously selected sensitizing dyes with complementary light absorption beyond the high eye-sensitivity region to increase the PCE as well as transparency. By utilizing a dye cocktail of yellow-coloured dye D-131 and green-coloured squaraine dye SQ-140 having 4 times higher molar extinction coefficient than D-131 in different molar ratios, the DSSCs were fabricated and analyzed. Transparent DSSC fabricated utilizing a dye cocktail of D-131 and SQ-140 dyes in a 9:1 molar ratio exhibited a PCE of 3.89 % and AVT of 36.9 %. To enhance the PCE further, a sequential dye-adsorption method was adopted leading to an enhancement in the J_{sc} from 8.99 mA/cm^2 to 14.15 mA/cm^2 as compared to its dye cocktail-based device counterpart. In the dye cocktail, the presence of inter-dye interaction hampered the light-harvesting, which was suppressed by utilizing the stepwise dye adsorption leading to an increase in PCE of 4.53 % from 3.89 %. Stepwise co-sensitized transparent DSSCs exhibited an AVT of 15.6 %, which is sufficient for good visual perception.

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